

GAS PHASE PYROLYSIS OF AZADIENES AND
RELATED COMPOUNDS

by

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Synthesis and Mechanism of Action of the β -Lactam Antibiotics (5 lectures), Glaxo Group Research Ltd.

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Abstract

Flash vacuum pyrolysis of 1,1-dimethyl-5-phenyl-diazapentadienes gives pyrroles as the main product in the pyrolysate. Substituted quinolines are found as minor products, due to a 6π electrocyclic ring closure followed by elimination. The pyrroles could be formed *via* an intramolecular hydrogen shift yielding a diradical intermediate which cyclises to the five membered ring followed by cleavage of the anilino radical and hydrogen or alkyl radical. Methyl groups on the carbon chain of the 1,5-diazapentadiene produced a higher ratio of quinolines compared with pyrroles. Pyrolysis of 5-phenyl-1,1,3-trimethyl-1,5-diazapentadiene also gave quinoline itself, due to an allowed 1,5-hydrogen shift making the cleavage of an alkyl group possible. This was confirmed by pyrolysis of the appropriate deuteriated compounds.

An extensive selection of hetero-2-azadienes have been pyrolysed and a 4π electrocyclisation followed by cleavage and elimination of nitrile, found to be general over a wide range of compounds. However, whenever the central bond becomes weak due to poor conjugative interaction between the two double bonds of the heterodiene, the thermolysis reactions are dominated by radical cleavage of this central bond. Another minor exception is when there is a dimethylamino group able to transfer a hydrogen to a remote *N*-phenyl group, leading to five membered ring products, analogous to the 1,1-dialkyl-5-phenyl-1,5-diazapentadiene thermolysis reactions.

Variable temperature ^1H n.m.r. spectroscopy has been

used to study many of the dimethylamino compounds as the restricted rotation of the dimethylamino groups gives information about the conjugation of these systems. The basic 1,1-dimethyl-5-phenyl-1,5-diazapentadiene was altered substantially to find the effect of replacing the *N*-phenyl group with other groups or atoms. The effect of nitrogen atoms in various positions of the pentadiene chain was also studied as was the influence of methyl substituents on the pentadiene chain.

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PUBLICATIONS

INTRODUCTION

A. Flash Vacuum Pyrolysis

Flash vacuum pyrolysis is a convenient method of carrying out many different high temperature reactions. It involves vaporisation of the substrate from an inlet system into a silica furnace tube, which can be maintained at temperatures up to 1000°C. The apparatus is kept under a vacuum of 10^{-2} - 10^{-3} Torr and the products are collected in a liquid nitrogen trap situated at the exit point of the furnace. A diagram of the apparatus and further details of the method may be found in the experimental section of this thesis.

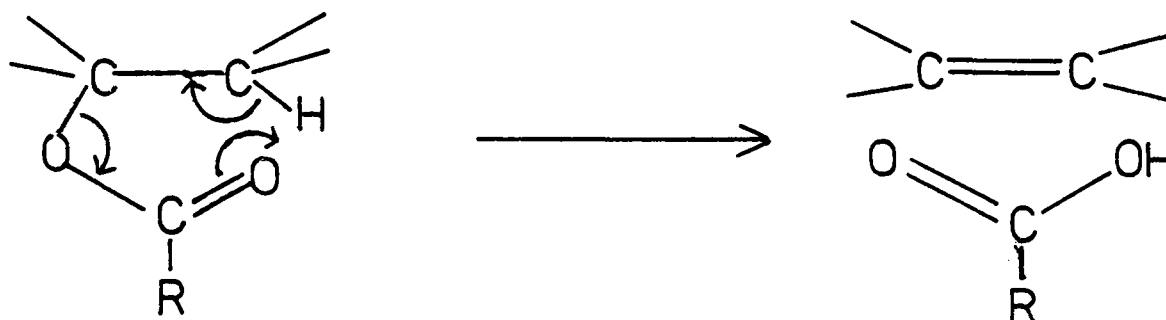
This technique ensures that the material has only a very short contact time in the hot zone - estimated to be in the order of 1-10 milliseconds. This, coupled with the very low concentration of the molecules in the hot zone at any one time, tends to result in intramolecular rather than intermolecular reactions taking place, although radical coupling reactions are observed. There have been many reviews on flash vacuum pyrolysis, the most comprehensive being Brown's recent monograph.¹ General reviews on the subject include those by de Mayo,² Seybold,³ Hageman and Wiersum,⁴ Wentrup,⁵ Vogtle and Rossa,⁶ Schaden⁷ and Wiersum.⁸⁻¹⁰

There are several types of reaction that may occur during flash vacuum pyrolysis. These include generation of transient species such as free radicals, arynes, carbenes, nitrenes etc., elimination and fragmentation reactions. Any of these may be followed by thermal rearrangement of the resulting molecule. The subject of thermal isomerisation

of hydrocarbons has been well documented by Gajewski.¹¹

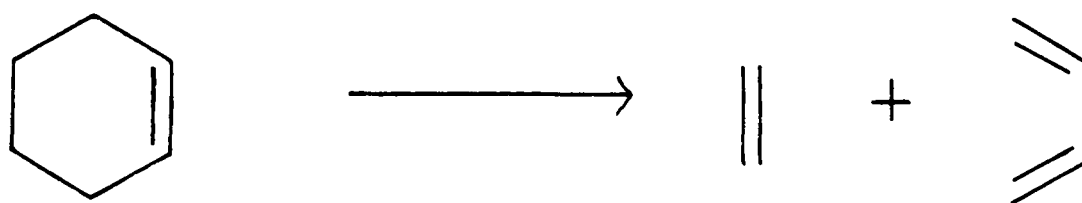
The two major classes of reaction undergone during flash vacuum pyrolysis are concerted reactions and those involving loss of a small molecule to give either carbene type species or diradicals.

For example, much work has been carried out on the pyrolytic *cis* elimination reactions, mainly involving esters, and this subject has been reviewed by DePuy and King,¹² Maccoll¹³ and Smith and Kelly¹⁴. Pyrolysis of esters generally results in loss of the ester linkage to give good yields of alkenes by a cyclic, concerted process (Scheme 1) - first proposed by Hurd and Blunck.¹⁵



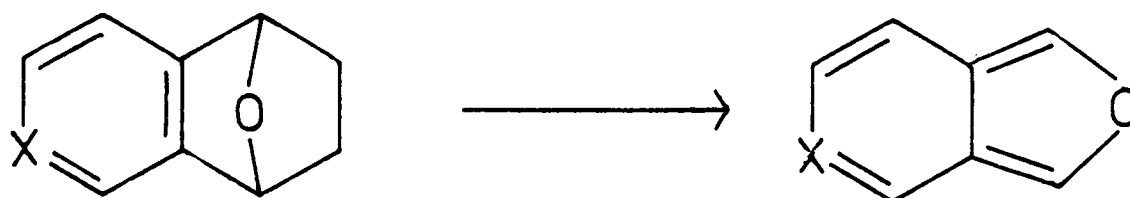
Scheme 1

The Retro-Diels Alder reaction may also occur during flash vacuum pyrolysis. For example, Kistiakowsky¹⁶ has decomposed cyclohexene to give butadiene, as shown in Scheme 2.



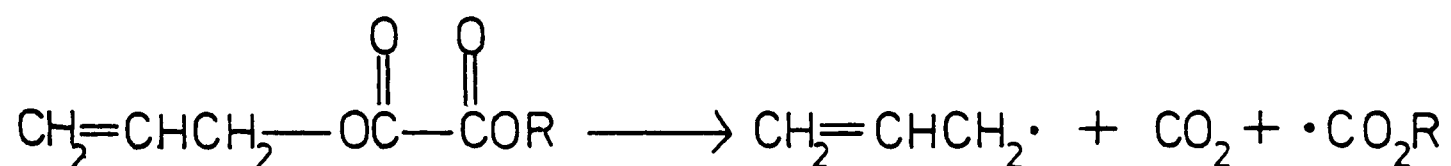
Scheme 2

Similarly, Wiersum has found flash vacuum pyrolysis to be a very useful preparative route to isobenzofuran¹⁷ and furo-pyridine¹⁸ *via* a Retro-Diels Alder reaction (Scheme 3).



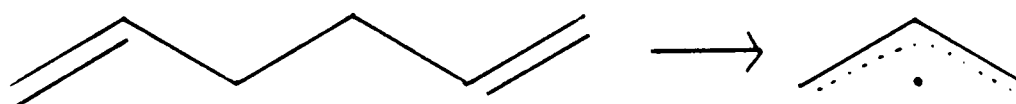
Scheme 3

Pyrolysis can also be used for the formation of carbon radicals. For example, the pyrolytic decomposition of diallyl or allyl alkyl oxalates proceeds as shown in Scheme 4, to give an allyl radical.



Scheme 4

Maier¹⁹ has shown how flash vacuum pyrolysis can be used, in conjunction with matrix isolation, to generate and then study (by IR, UV and ESR spectroscopy) very reactive species.

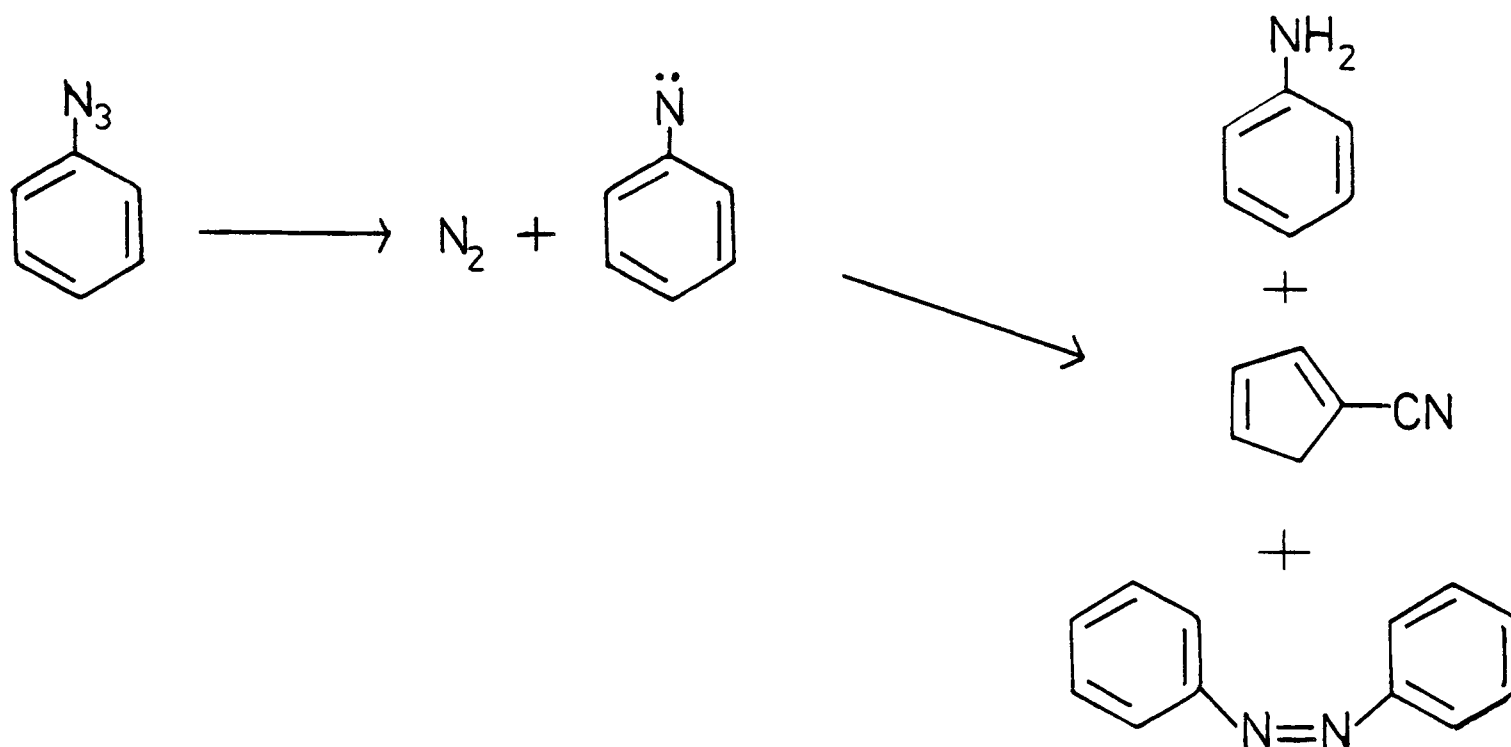


Scheme 5

A review of the generation of free radicals by pyrolysis is being prepared by Cadogan, McNab and Hickson.²⁰

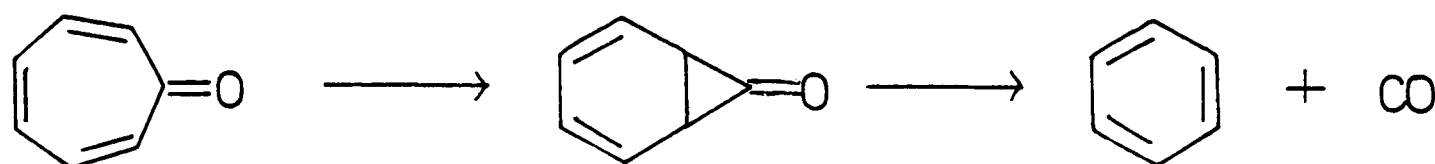
The generation and rearrangement of aromatic carbenes and nitrenes by gas phase pyrolysis has been reviewed in

considerable detail by Wentrup.²¹ Generation of transient species by flash vacuum pyrolysis is useful, in that intramolecular reactions tend to occur and the possibility of the reactive species interacting with any coordinated species or with the solvent, as may occur in solution, is ruled out. Phenyl nitrenes are generated directly from phenyl azide, with a typical reaction being as shown in Scheme 6.^{22,23}



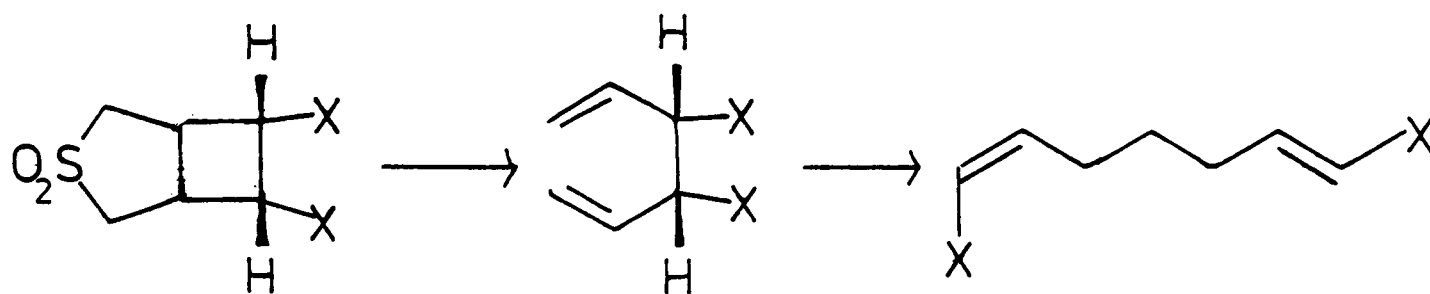
Scheme 6

Elimination of small molecules from cyclic structures can also take place by flash vacuum pyrolysis, eg. Scheme 7.^{4,24}



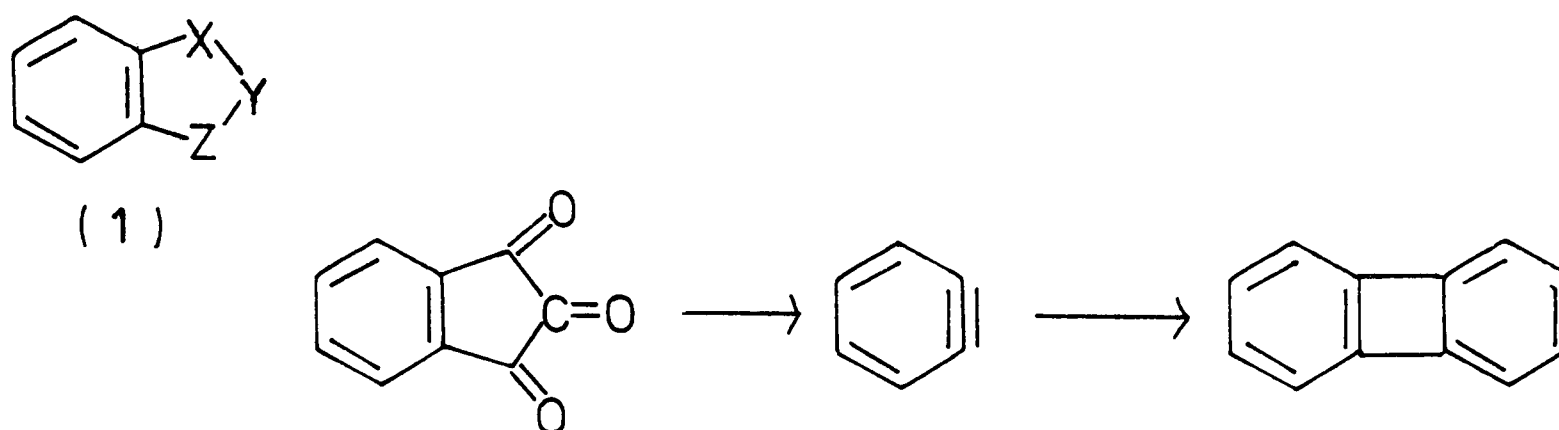
Scheme 7

The thermal extrusion of sulphur dioxide in this manner has been found to be a very useful step in the stereospecific synthesis of *E,Z*-1,5-dienes (Scheme 8).^{25,26}



Scheme 8

Arynes can be generated in the gas phase from a variety of ordinarily stable precursors of the general structure (1), in which X,Y and Z represent groups which can lead to thermodynamically highly stable fragments such as CO, CO₂, N₂ and SO₂,^{27,28} eg. Scheme 9.



Scheme 9

More recently this has been applied to the generation of five membered hetarynes²⁹ (Scheme 10).



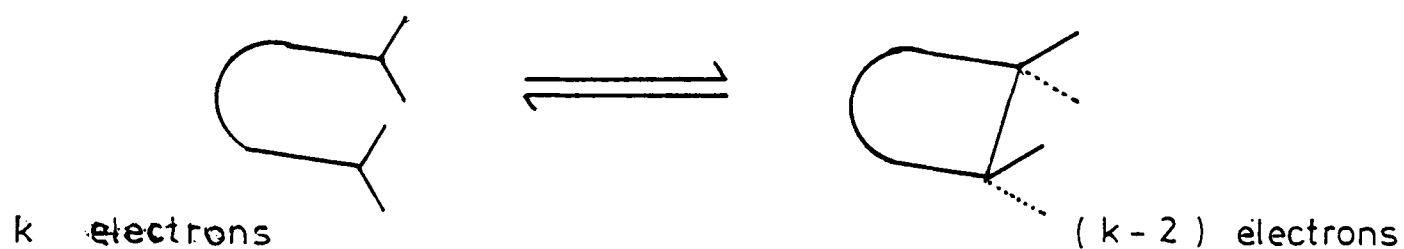
Scheme 10

Flash vacuum pyrolysis can also be used for the intramolecular rearrangement of molecules and these type of reactions form a major part of this thesis, and are discussed in greater detail in the rest of this chapter.

B. ELECTROCYCLIC REACTIONS

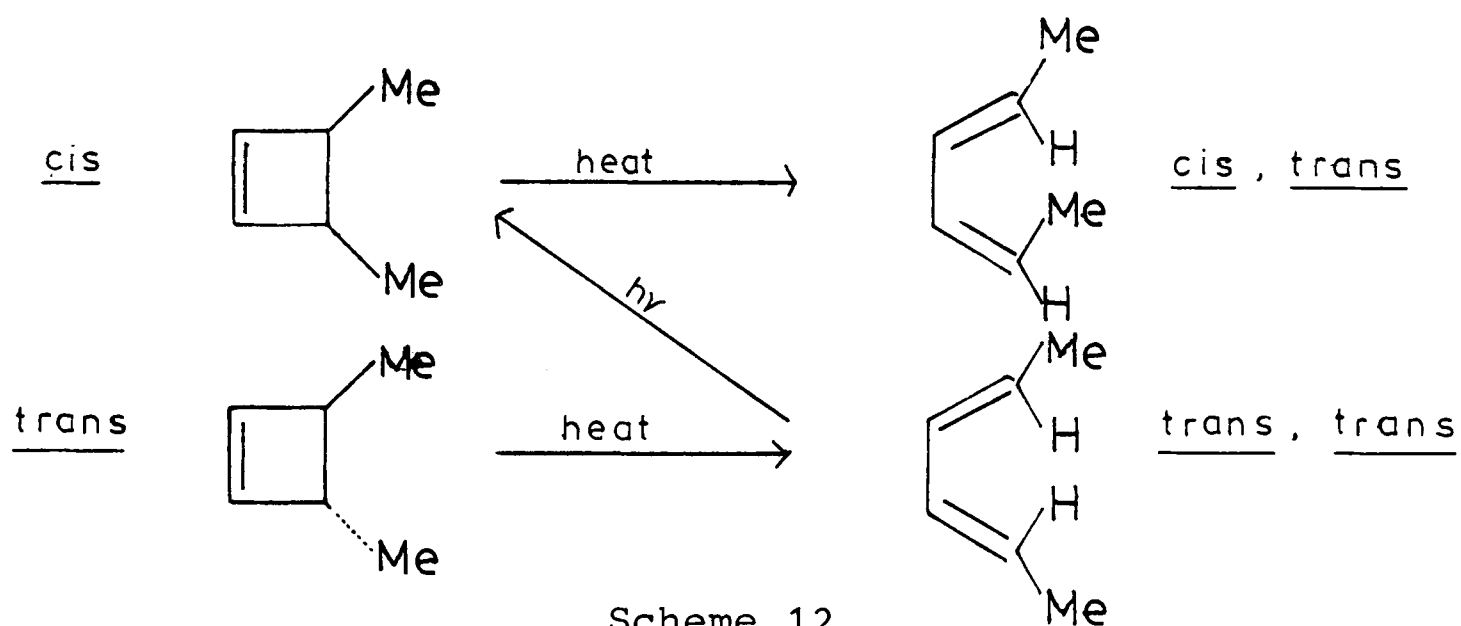
I. THEORY

An electrocyclic reaction is the formation of a σ bond between the termini of a linear π system, or the reverse, (Scheme 11).



Scheme 11

Consider, for example the interconversion of 3,4-dimethylcyclobutene and 2,4-hexadiene (Scheme 12). The *cis* cyclobutene yields only one of the three possible isomeric dienes and the *trans* cyclobutene yields a different isomer. The

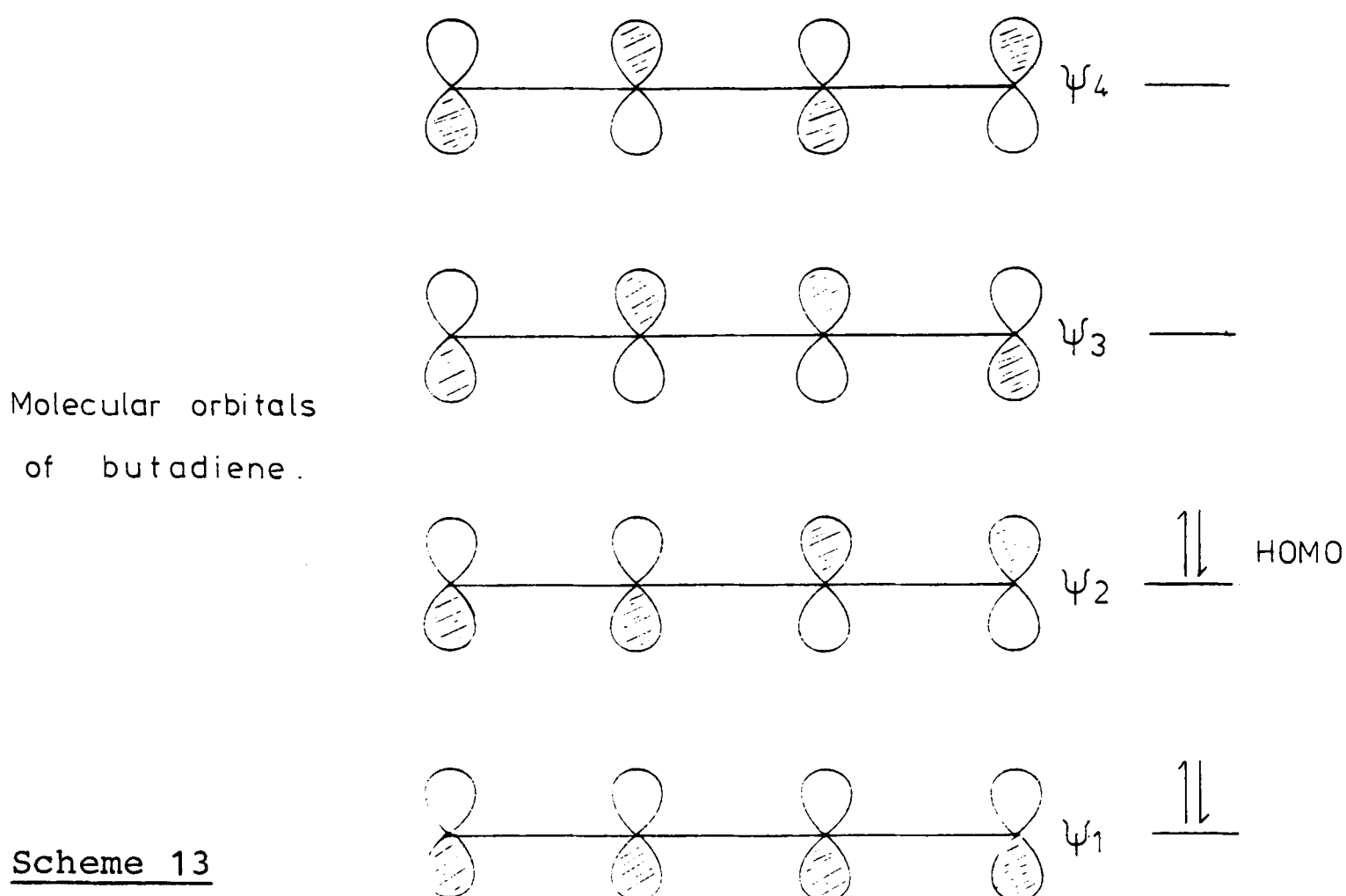


Scheme 12

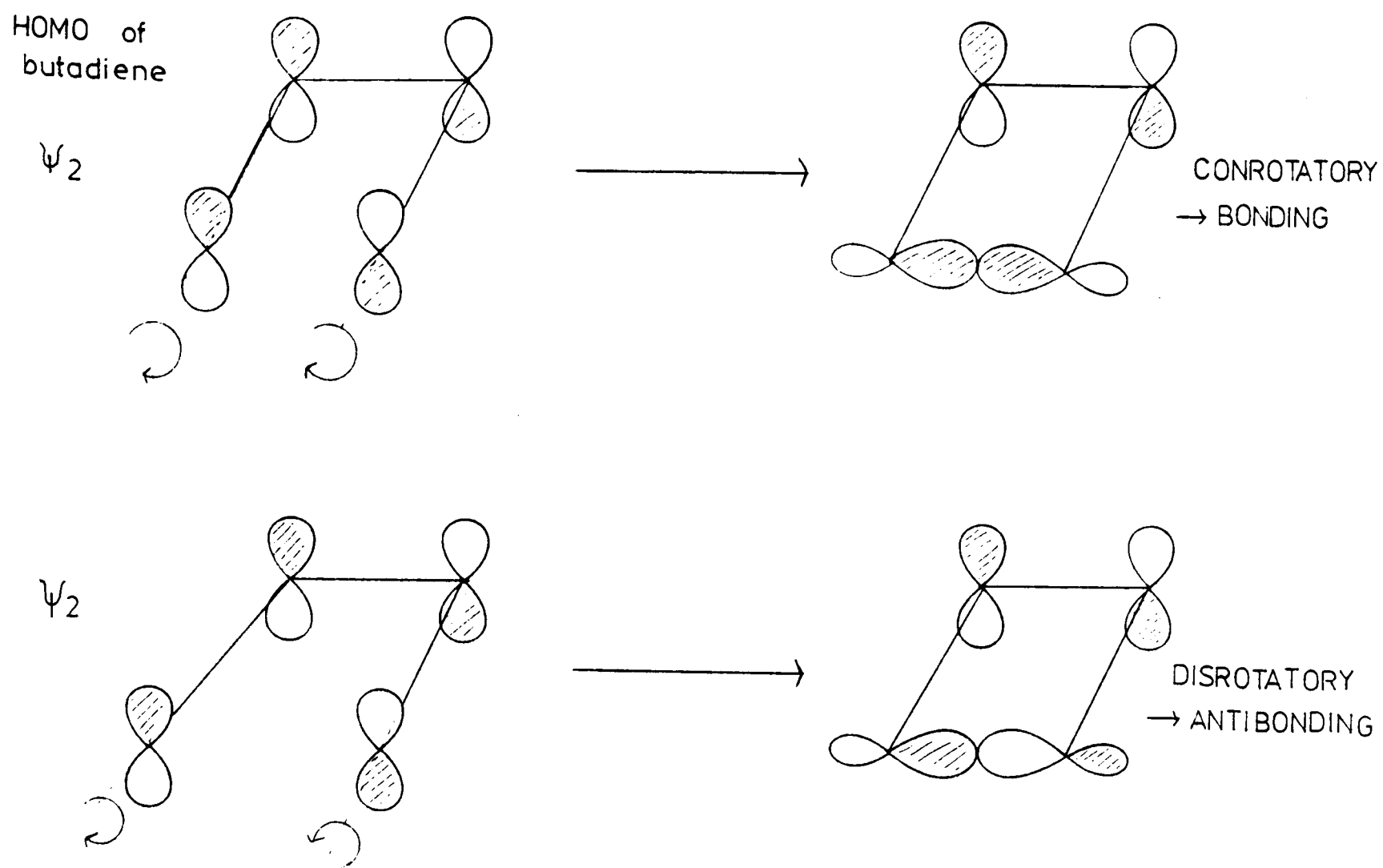
reaction is completely stereospecific. Furthermore, photochemical cyclisation of the *trans,trans* diene gives a different cyclobutene than the one from which the diene is formed by the thermal ring opening.

The exact stereochemistry of electrocyclic reactions depends upon the number of π electrons in the polyene and on whether the reaction is thermal or photochemical. This is accounted for by the orbital symmetry approach put forward by Woodward and Hoffmann^{30,31,32} in 1965.

In cyclisation, the two π electrons in the highest occupied molecular orbital (HOMO) form the new σ bond of the cycloalkene (Scheme 13).



Considering a disubstituted conjugated diene as shown in Scheme 12, the HOMO is ψ_2 and the electrons in this orbital will form the bond that closes the ring. Bond formation requires overlap, in this case overlap of lobes on C-1 and C-4 of the diene. To bring these lobes into position for overlap there must be rotation about two bonds, C_1-C_2 and C_3-C_4 . This rotation can take place in either a conrotatory or disrotatory fashion (Scheme 14).



Scheme 14

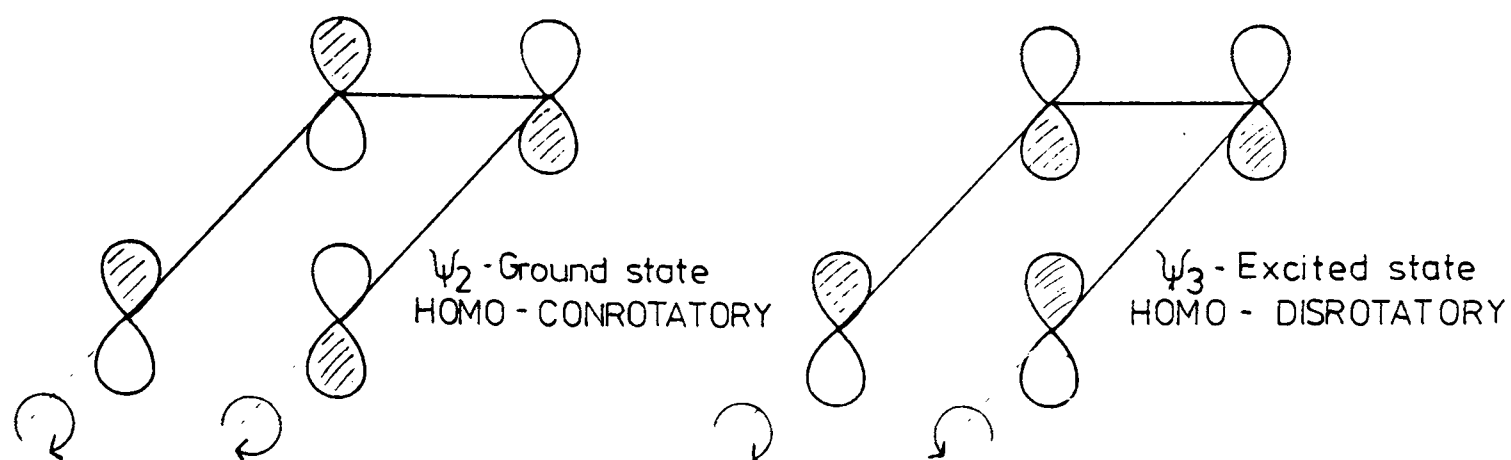
In this case conrotatory motion brings together lobes of the same phase; overlap occurs and a bond forms.

The principle of microscopic reversibility states that the stereochemistry of the reaction is the same in both directions, ie. cyclisation or ring opening. The reverse conrotatory electrocyclic change of a cyclobutene to a butadiene is a very well known process^{33,34} with its stereochemistry being established in 1958.

It is worth noting that where a conrotatory motion takes place, a 2-fold axis of symmetry is maintained throughout the change, whereas with a disrotatory motion, a plane of symmetry is held throughout the change.

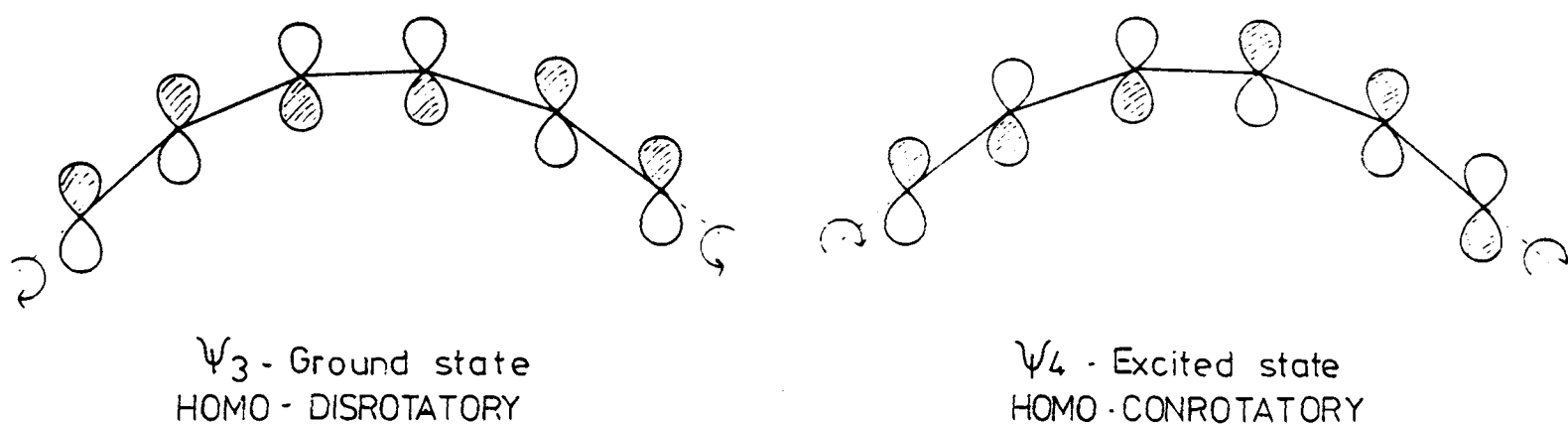
The photochemical reaction has the opposite stereochemistry due to the fact that butadiene is converted into an excited

state ie. one electron from ψ_2 is raised to ψ_3 . The HOMO is now ψ_3 and it is disrotatory motion that brings together lobes in the same phase (Scheme 15).



Scheme 15

For the thermal cyclisation of a disubstituted hexatriene, ψ_3 is the HOMO and disrotatory motion leads to bonding. However in a photochemical reaction ψ_4 is the HOMO and conrotatory motion is required (Scheme 16).



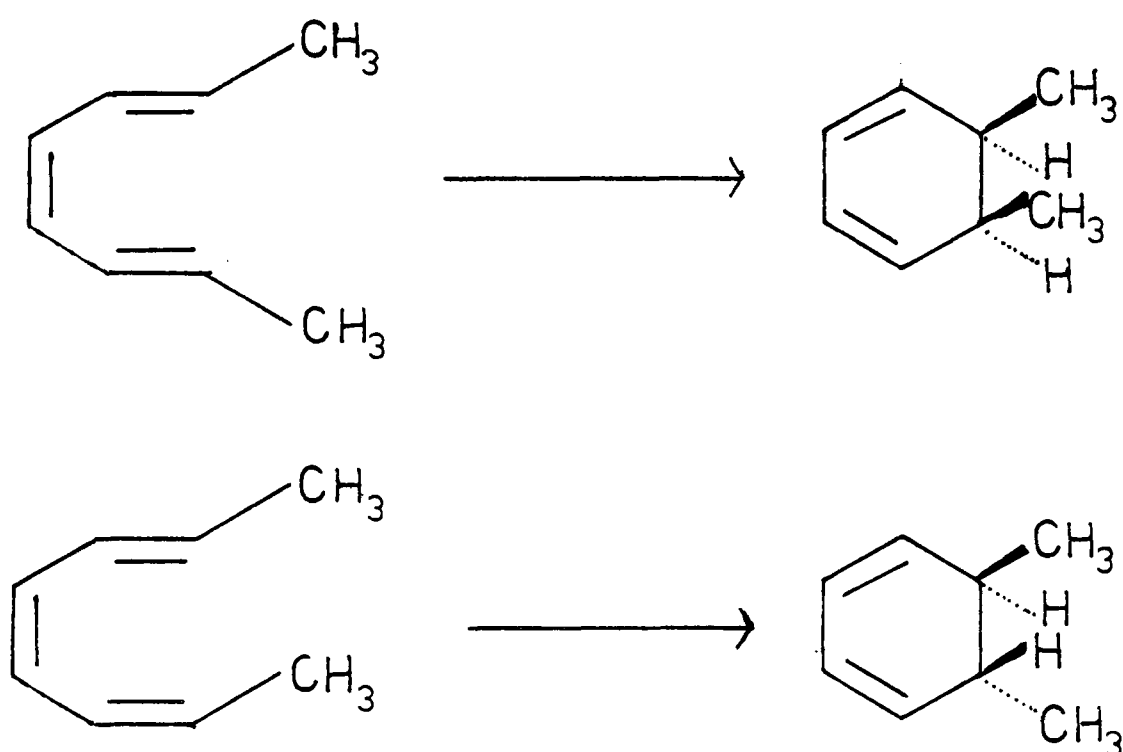
Scheme 16

A regular pattern emerges (see Table 1) which agrees with the fundamental principle of Woodward and Hoffmann. That is, that during a concerted process, the symmetry of the molecular orbitals involved in the reaction is conserved.

Table 1

<u>No. of π electrons</u>	<u>Reaction</u>	<u>Motion</u>
$4n$	thermal	conrotatory
$4n$	photochemical	disrotatory
$4n+2$	thermal	disrotatory
$4n+2$	photochemical	conrotatory

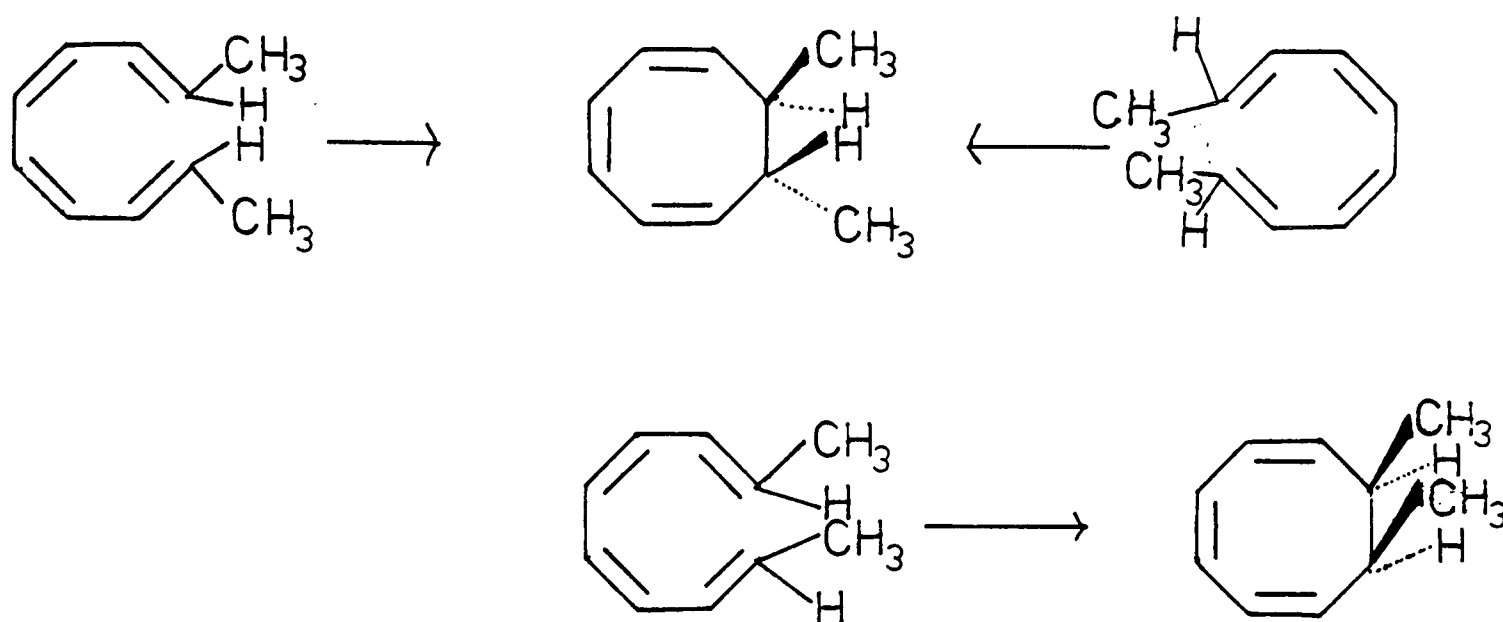
There are many examples in the literature which confirm the theory put forward by Woodward and Hoffmann. For instance, the thermal cyclisation of trienes has been shown to be disrotatory by the study of simple model compounds (Scheme 17).^{35,36,37}



Scheme 17

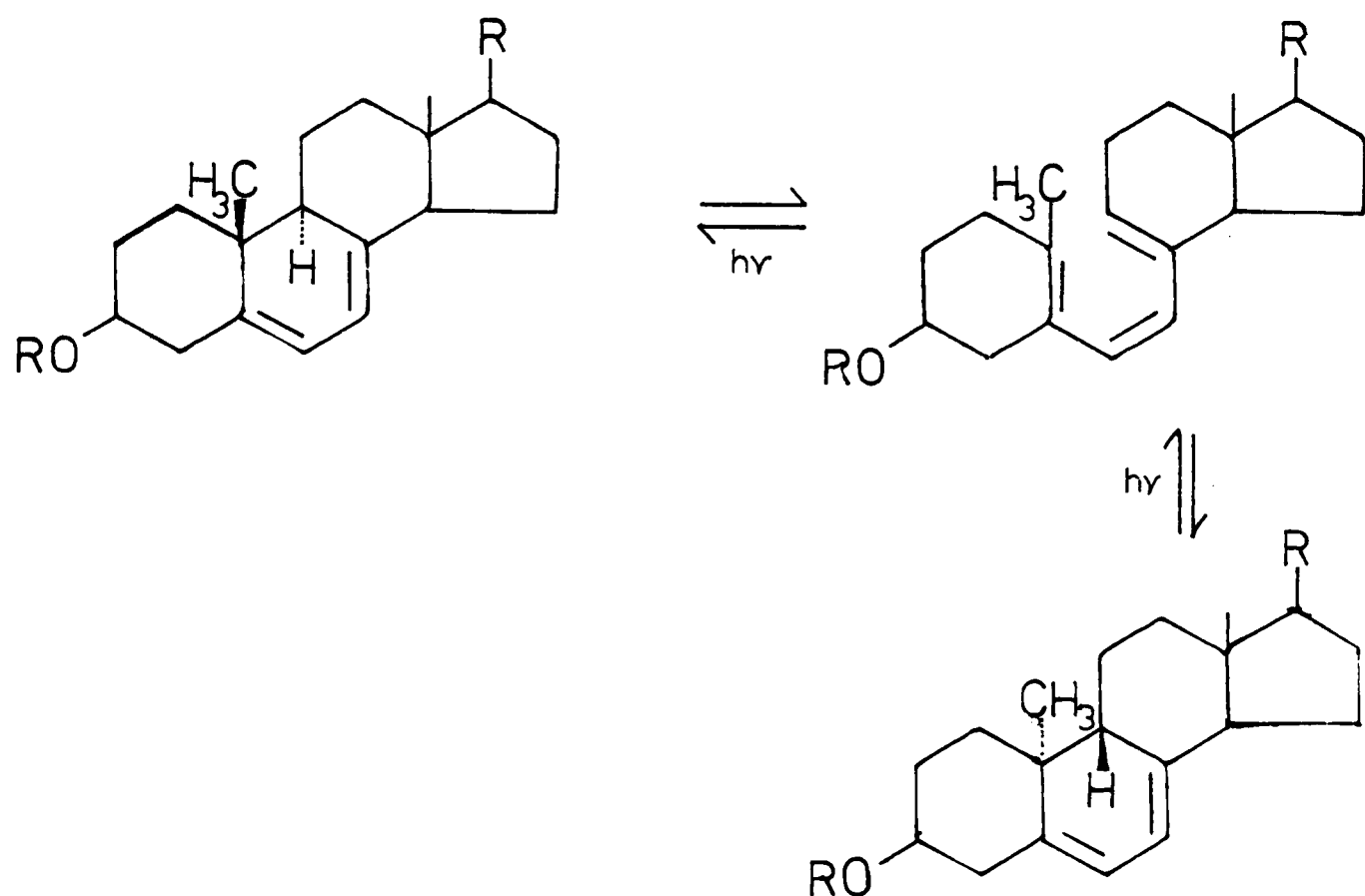
The thermal electrocyclic closure of a *cis,cis*-octatetraene should be conrotatory. Though *cis,cis*-octatetraene is far from planar, the same nodal patterns in the orbitals are preserved. The predicted stereochemical course for the

thermal reaction has been confirmed³⁸ (Scheme 18).



Scheme 18

The symmetry allowed photochemical conrotatory cyclisation of *cis*-hexatrienes, and the reverse reaction, were first recognised in studies in the vitamin D field³⁹ (Scheme 19).



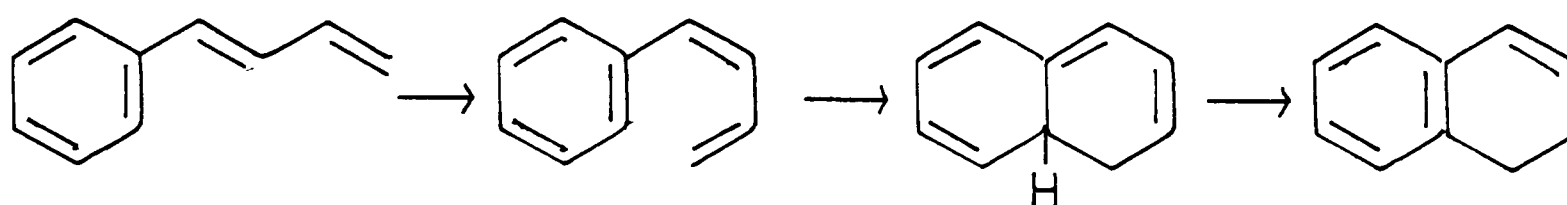
Scheme 19

Many thermal electrocyclic reactions are discussed in more detail in later sections of this thesis. However, in most cases the stereochemistry is lost in the reaction, but it is assumed that the reactions still follow Woodward and Hoffmann's theory on the conservation of orbital symmetry.⁴⁰

II. PYROLYTIC 6 π ELECTROCYCLIC REACTIONS

1. Ring Closure in the Gas Phase

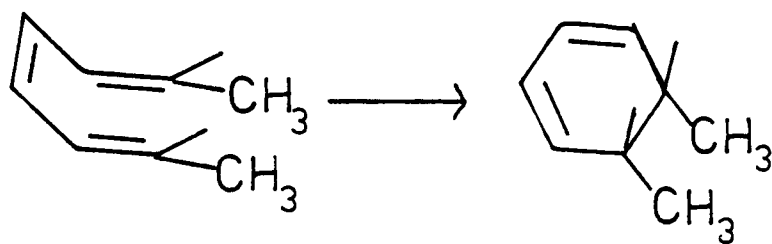
Weber *et al.*⁴¹ have found that gas phase pyrolysis of *trans*-1-phenyl-1,3-butadiene at 450°C yielded 1,2-dihydronaphthalene in good yield along with small quantities of *cis*-1-phenyl-1,3-butadiene and naphthalene, (Scheme 20). Under more vigorous conditions, naphthalene is formed instead of dihydronaphthalene, therefore pyrolysis conditions are quite critical.



Scheme 20

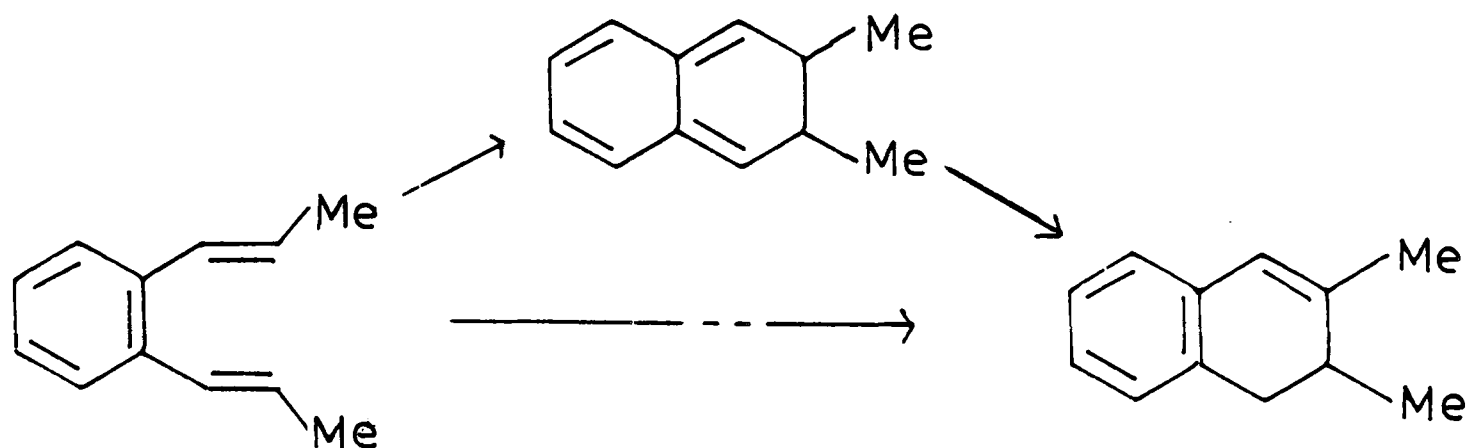
The formation of 1,2-dihydronaphthalene from *trans*-1-phenyl-1,3-butadiene has been rationalised by Weber by a three step reaction sequence. The first step is the isomerisation of *trans*-1-phenyl-1,3-butadiene to the *cis*-isomer which has the proper geometry to undergo the electrocyclic reaction

converting a conjugated triene into a 1,3-cyclohexadiene. This reaction would be expected to take place in a thermally allowed disrotatory fashion, but the final step of the sequence (Scheme 20) is a 1,5-hydrogen shift which destroys the stereochemistry at the reaction site. The triene undergoing this reaction is composed of the two double bonds of the 1,3-butadiene and one double bond of the benzene ring. Weber suggests that the high energy of activation required for the reaction reflects the loss of benzenoid resonance energy in the intermediate. A comparison between *trans,cis,trans*-octa-2,4,6-triene which is converted to *cis*-5,6-dimethyl cyclohexa-1,3-diene at 130°C³⁷ (Scheme 21) and this case where *trans*-1-phenyl-1,3-butadiene does not yield 1,2-dihydronaphthalene till 400°C, may reflect this loss of aromatic stabilisation. However, an alternative explanation may be the energy required for the *trans*→*cis* isomerisation.



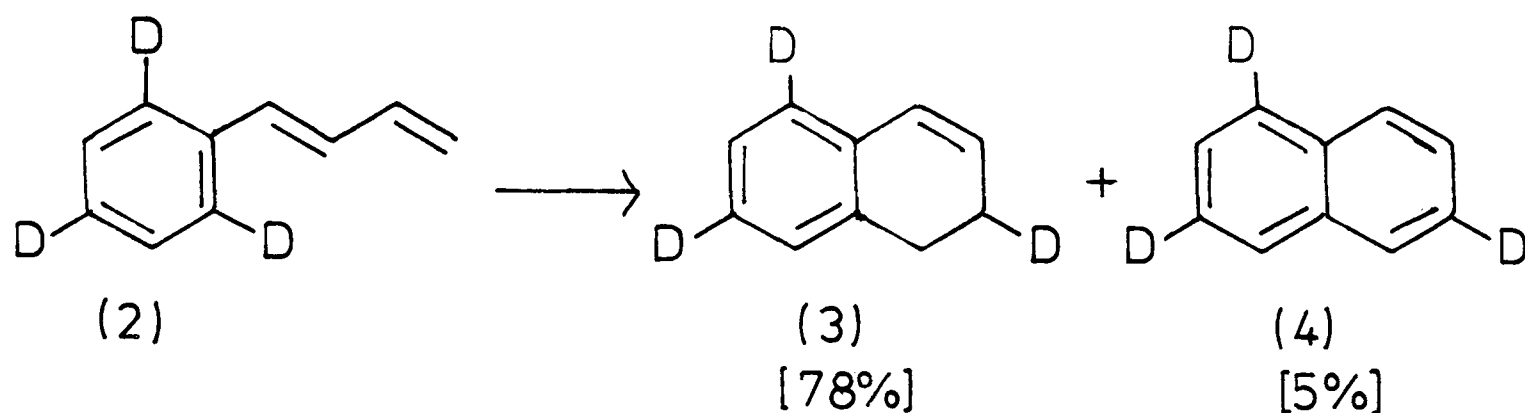
Scheme 21

A related example of participation of a double bond from a benzene ring in an electrocyclic reaction is the pyrolysis in solution of 1,2-dipropenyl benzene to give 2,3-dimethyl-1,2-dihydronaphthalene,⁴² (Scheme 22). The final step in both the reaction sequences (Schemes 20 and 22) would be a symmetry

Scheme 22

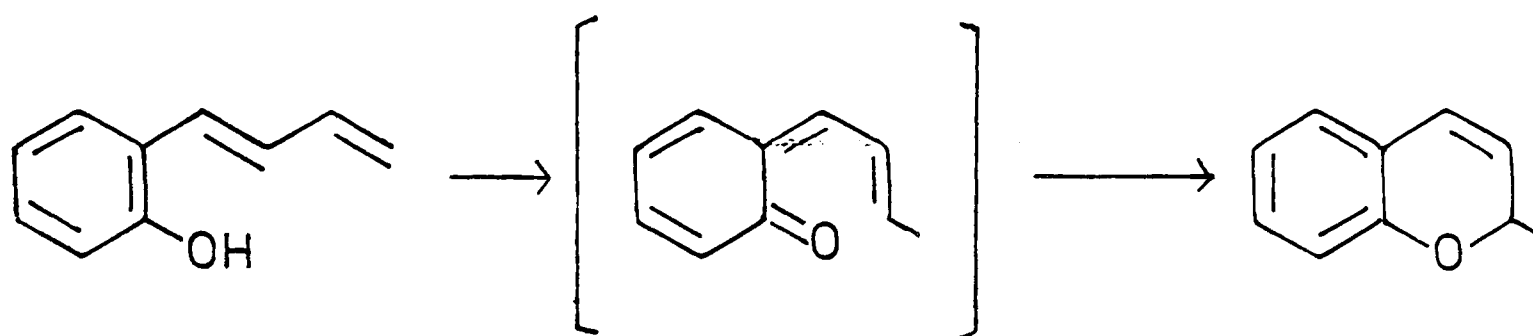
allowed 1,5-suprafacial sigmatropic hydrogen migration leading to restoration of the aromatic nucleus.

The proposed mechanism has been tested⁴¹ by the pyrolysis of the deuteriated phenylbutadiene (2) which gave the pre-

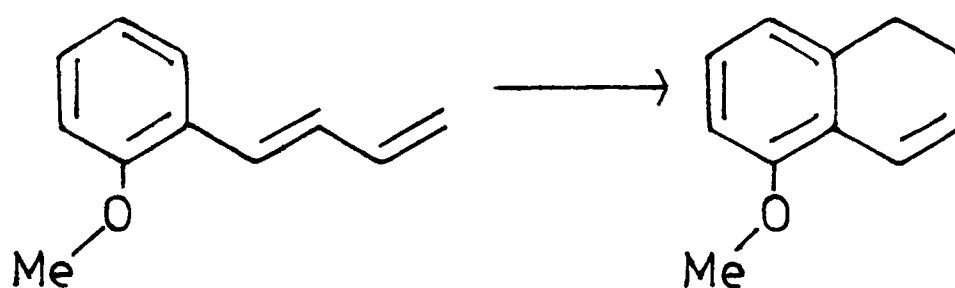
Scheme 23

dicted dihydronaphthalene (3) in 78% yield, as well as naphthalene-1,3,6-d₃ (4) - (5%).

Previous work^{43,44} had shown that the product of pyrolysis of 1-(*o*-hydroxyphenyl)-1,3-butadiene was not 1,2-dihydro-5-naphthol but rather 2-methylchromene (Scheme 24).

Scheme 24

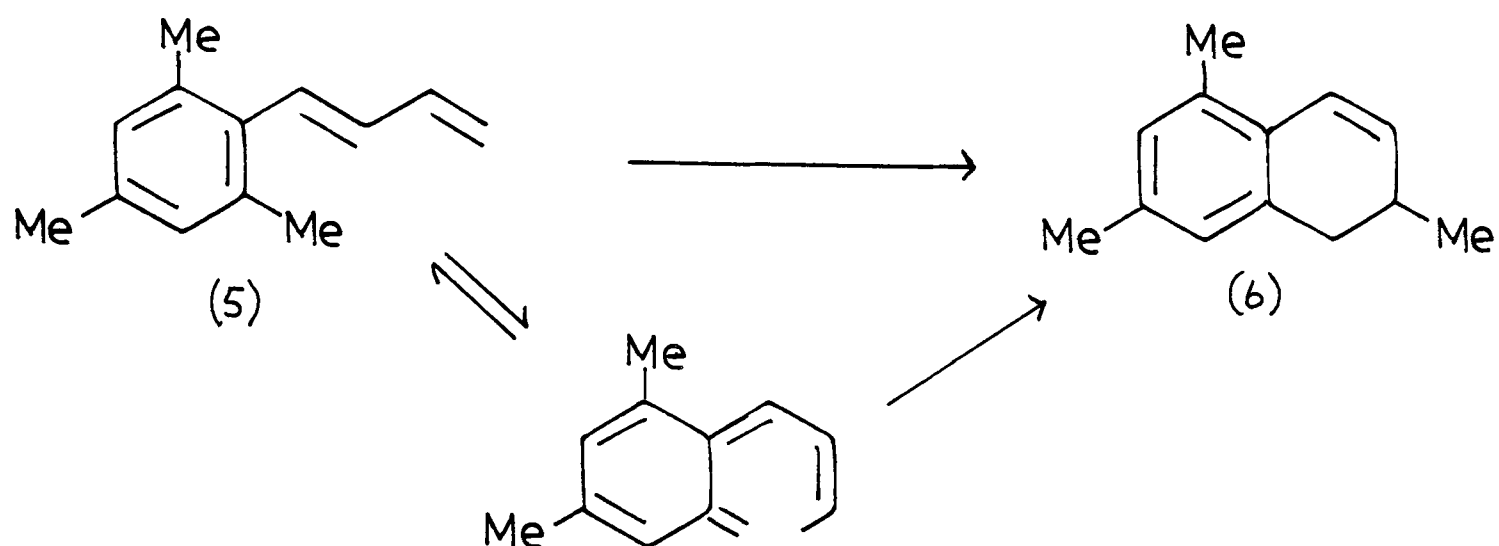
The result was explained by an initial 1,7-sigmatropic hydrogen shift to yield an *w*-vinyl-*o*-quinomethide intermediate which undergoes electrocyclic ring closure to give 2-methylchromene. The ability of the reaction to tolerate a methoxy substituent, at least in the ortho position, was therefore not clear.

Scheme 25

However, Weber⁴⁵ found that the gas phase pyrolysis reaction of 1-(2'-methoxyphenyl)-1,3-butadiene yields 5-methoxy-1,2-dihydronaphthalene (Scheme 25). Therefore this result is consistent with the three step mechanism previously proposed to account for the formation of 1,2-dihydronaphthalene on pyrolysis of 1-phenyl-1,3-butadiene in the gas phase. Previous syntheses of *w*-methoxy-1,2-dihydronaphthalene (*w* = 5,6,7 or 8) isomers have utilised a variety of reactions since no one reaction was generally applicable.

trans-1-Mesityl-1,3-butadiene (5) has also been pyrolysed⁴¹

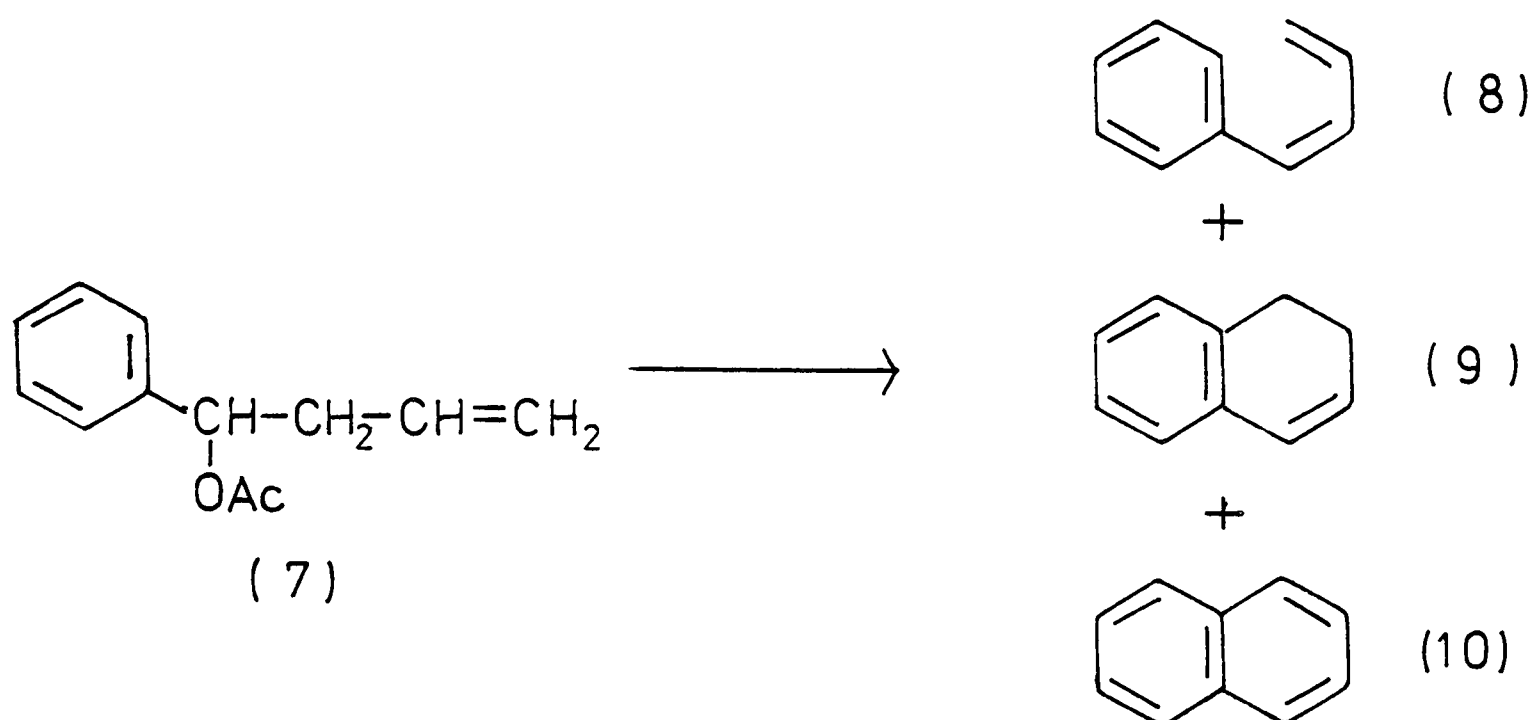
and gave the predicted product, 2,5,7-trimethyl-1,2-dihydronaphthalene (6). In this case the reaction may involve a



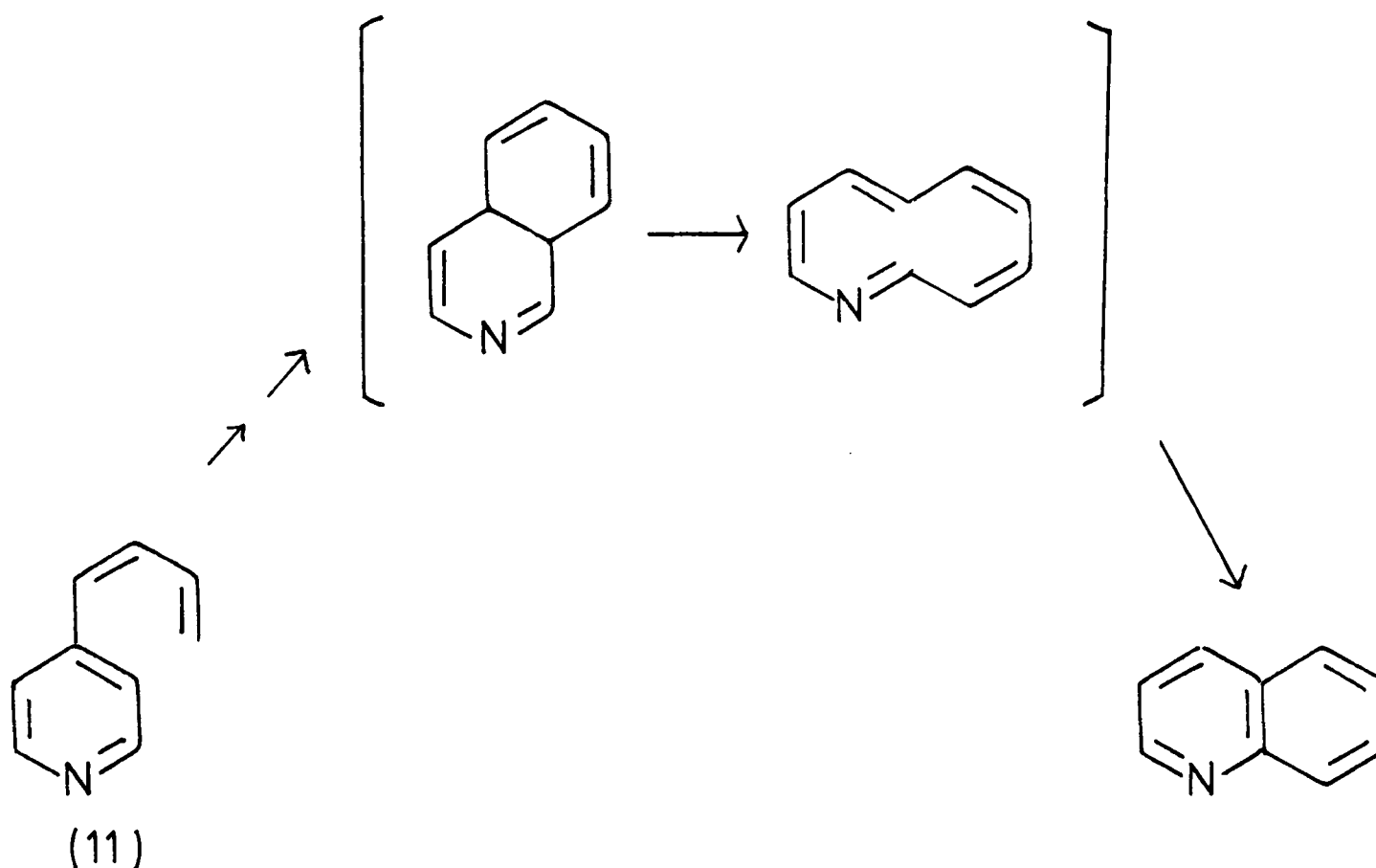
Scheme 26

suprafacial 1,5-sigmatropic rearrangement of a methyl group rather than a hydrogen. Alternatively, a 1,7-sigmatropic hydrogen migration followed by an electrocyclic reaction of the triene thus generated, may take place. By labelling the methyl groups, one would be able to show which of the two possibilities was occurring.

In 1969, flash thermal cyclisation at 500-900°C of 1-arylbut-3-enyl acetates was reported,⁴⁶ in which the butadiene function was generated *in situ*.

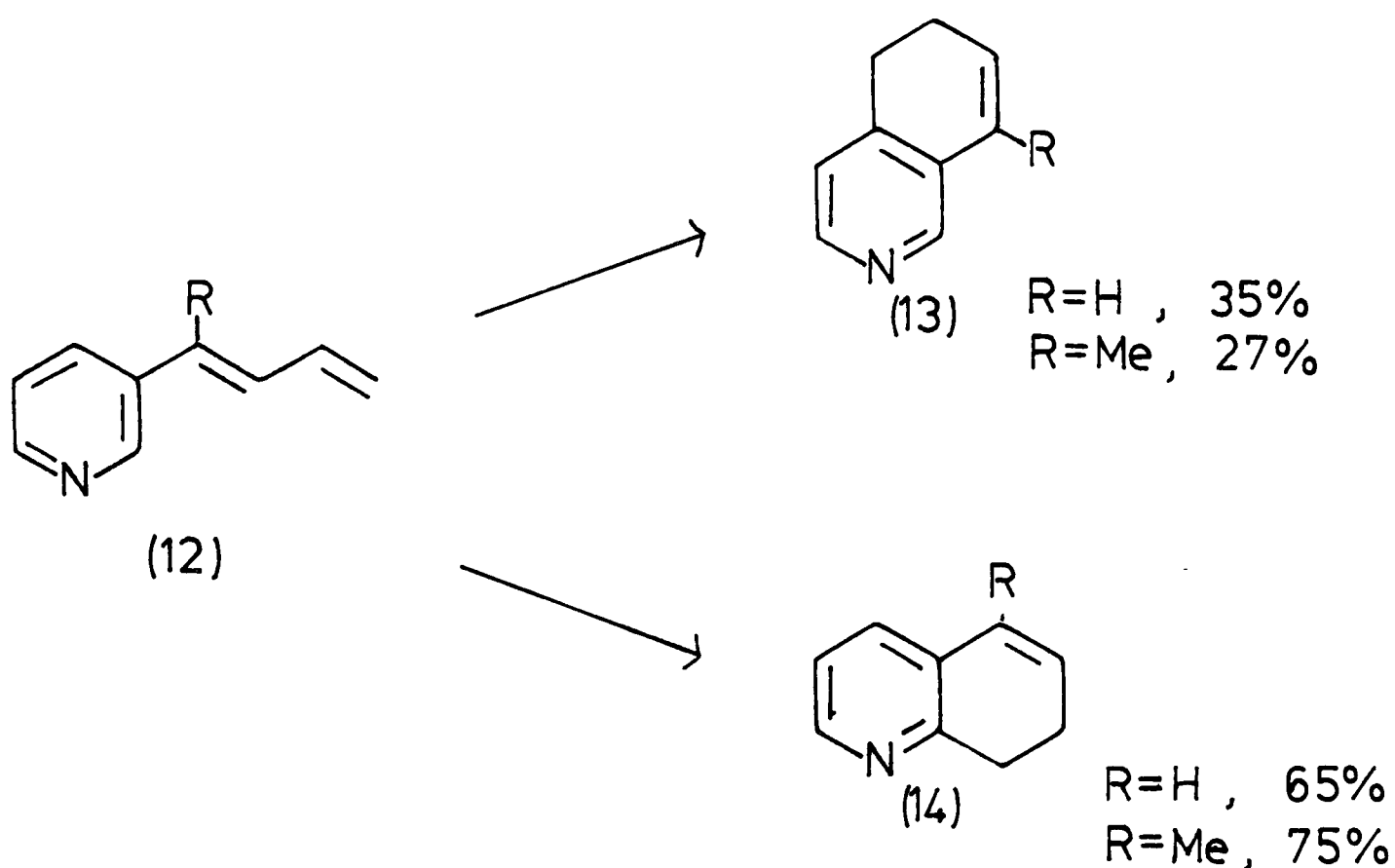
Scheme 27

When a solution of 1-arylbut-3-enyl acetate (7) in benzene was flash pyrolysed through a quartz tube at 500-900°C, elimination of acetic acid occurred to give the corresponding 1-aryl-butadiene (8) as expected, together with its cyclised derivatives (9) and (10). However, when 4-pyridylbut-3-enylacetate (11) was pyrolysed under similar conditions, quinoline was observed as well as the expected isoquinoline (Scheme 28).

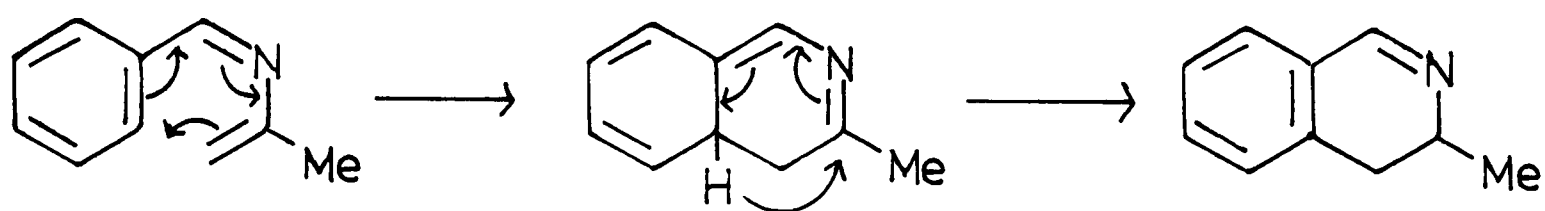


Scheme 28

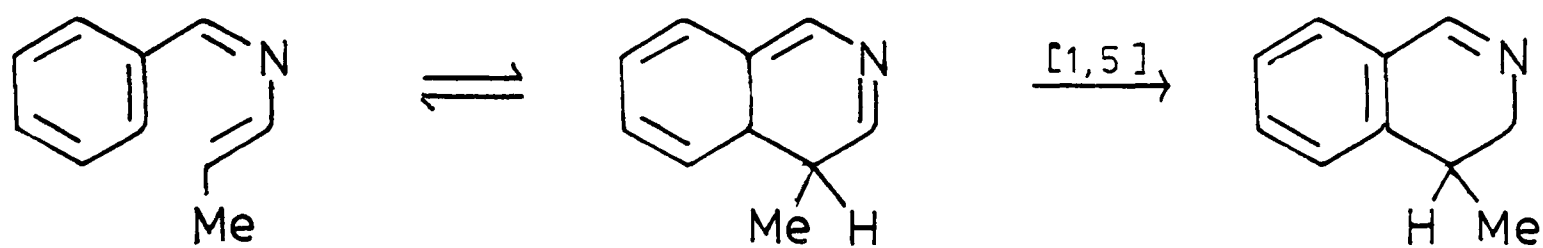
Yoshida⁴⁶ has suggested that a 10-membered ring intermediate may be involved. A general synthesis of 5,6- and 7,8-dihydroquinolines (and dihydroisoquinolines) has also been reported by Weber⁴⁷ based on joining a specific partially reduced aromatic ring on to a pyridine ring. Compound (11) has been pyrolysed and only the expected isoquinoline was observed, with no quinoline present, possibly due to the lower temperature used.

Scheme 29

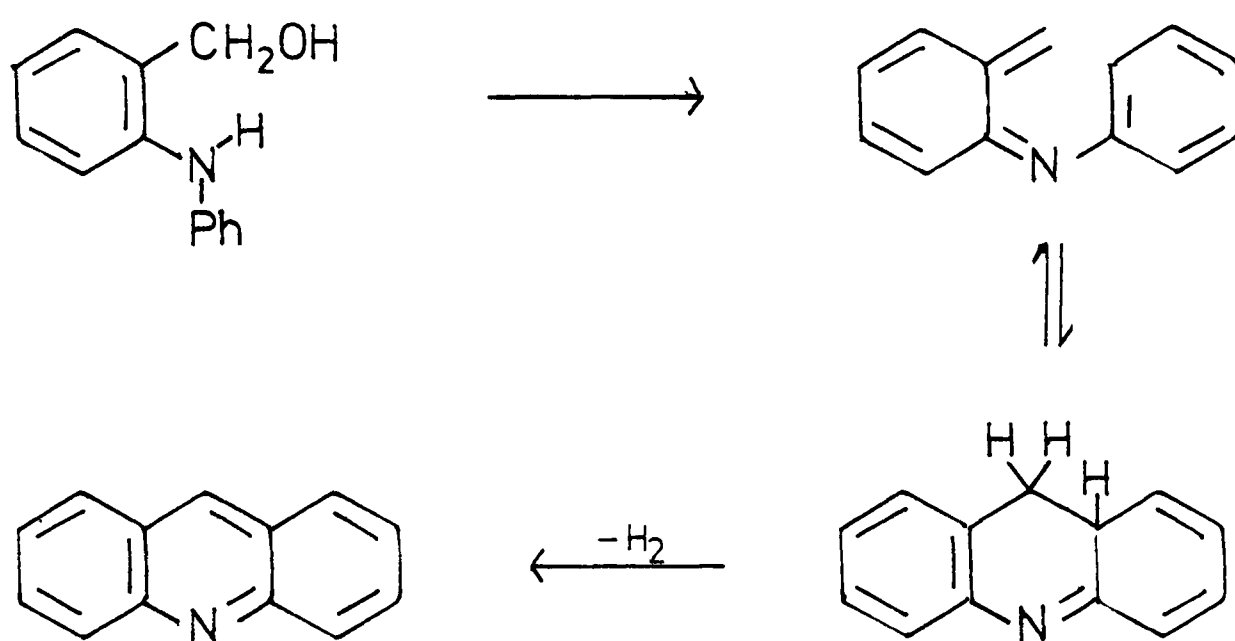
1-Methyl-1-(*w*-pyridinyl)-1,3-butadiene (12) was also pyrolysed in the gas phase, and gave a mixture of (13) and (14) in a ratio of 1:2.

Scheme 30

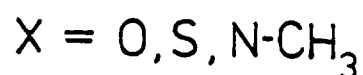
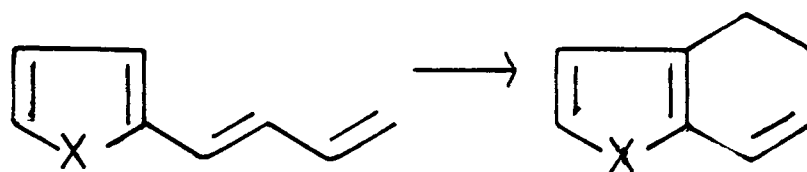
Azabutadienes have been found by Wendling and Bergman⁴⁸ to undergo the same electrocyclic ring closure in the gas phase, followed by a 1,5-hydrogen migration, to give dihydroisoquinolines (Scheme 30). Taylor and Govindan⁴⁹ have reported an almost identical reaction (Scheme 31).

Scheme 31

A similar reaction takes place when *o*-(hydroxymethyl)anilines are gas phase pyrolysed.⁵⁰ This is found to be a simple convenient method of producing nitrogen analogues of *o*-xylylenes (Scheme 32).

Scheme 32

Weber⁵¹ has also extended the reaction to the synthesis of 4,5-dihydrobenzo[b]furans, 4,5-dihydro[b]thiophenes and 4,5-dihydroindoles, again with an electrocyclic gas phase reaction from the appropriate 1,3-butadiene (Scheme 33).

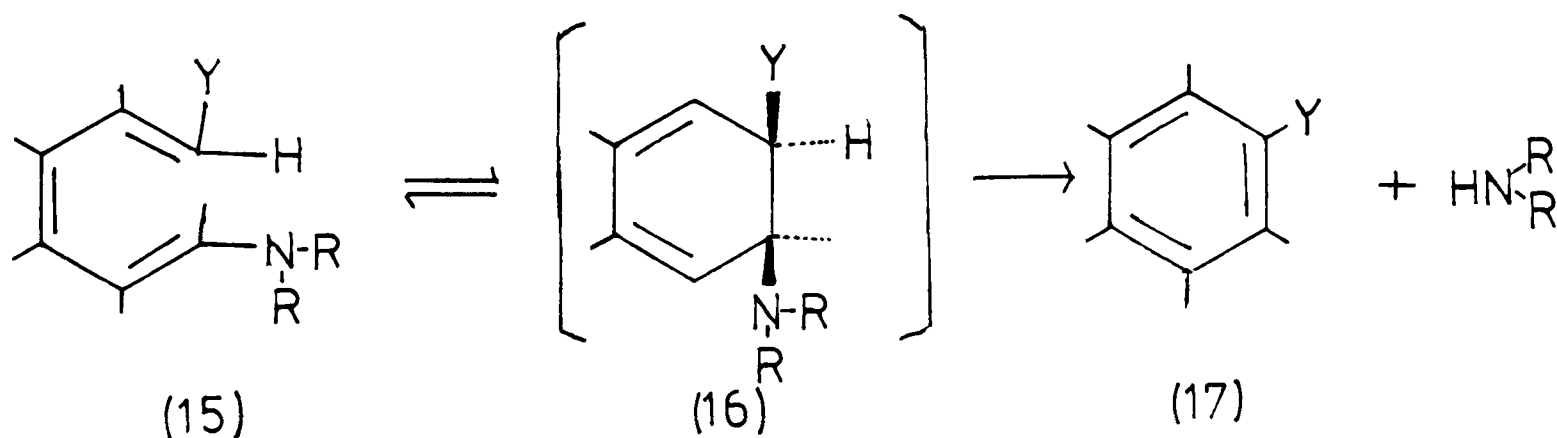


Scheme 33

He found that the pyrolysis conditions were critical (particularly pressure), as pyrolysis of 1-(2'-furyl)-1,3-butadiene has been reported⁴⁶ to yield a mixture of 4,5- and 6,7-dihydrobenzo[b]furans and benzo[b]furan. Likewise, pyrolysis of 1-(2'-thienyl)-1,3-butadiene has been reported to yield a mixture of 4,5- and 6,7-dihydrobenzo[b]thiophenes and benzo[b]thiophene.

2. Ring Closure with Elimination in Solution

Jutz⁵² has comprehensively reviewed a recently developed method to synthesise a wide range of oligo- and polycyclic aromatics and heteroaromatics. The route to these compounds, which is surprisingly simple, is based on a thermal electrocyclic hexatriene-cyclohexadiene ring closure, combined with an elimination reaction (Scheme 34).

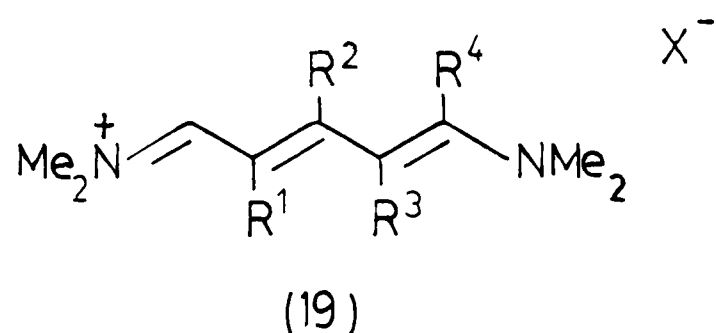
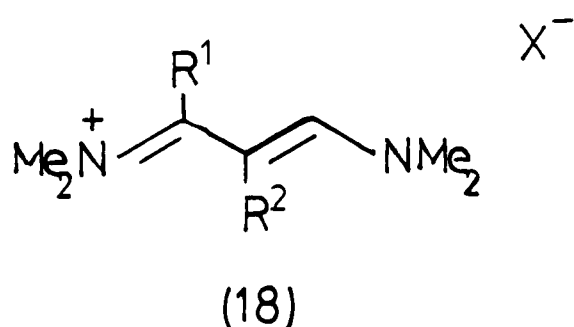


Scheme 34

1-Dialkylamino-1,3,5-hexatrienes form benzene derivatives by thermolysis, and with evolution of dialkylamine. The conformation and configuration of the trienamine (15) must be such that there is effective overlap of the orbitals at atoms 1 and 6 if ring closure is to take place. Steric interactions between substituents in the chain are able to shift the conformational and configurational equilibria in favour of structure (15). In such cases, the rate of reaction to (17) may be enhanced or the thermolysis temperature may be lowered. Conversely, however, factors impeding orbital overlap may prevent the cyclisation from taking place eg. steric overcrowding at positions 1 and 6 and all structural features producing an angle strain during ring formation.

The cyclisation is found to be general, in as far as one double bond of the 1-aminohexatriene may be part of an aromatic or heteroaromatic system and yet still cyclise smoothly. In addition, one or two carbon atoms in the chain of (15) may be replaced by nitrogen, finally forming a six-membered heteroaromatic ring.

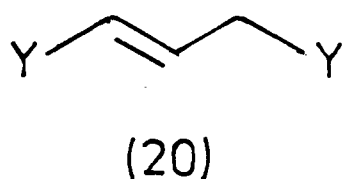
1-Aminohexatrienes are easy to obtain by Aldol- or Knoevenagel-like condensations of various 'vinamidinium salts' (18)⁵³ or their vinylogues (19), with a wide range of C-H acid methyl and methylene compounds.



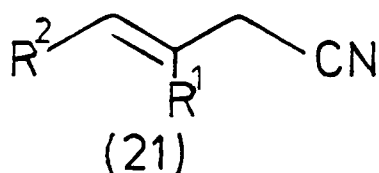
In a typical experiment, equimolar amounts of (18) or (19), and the C-H acid component are dissolved in a polar, high boiling solvent, usually quinoline, and sodium methoxide is added. The formation of (16) is indicated by the cleavage of nearly the theoretical amount of amine, however, in normal preparations (16) is not usually isolated. The temperature of the mixture is then raised and a second equivalent of amine is split off, leaving the cyclised product.

The type of compounds that can undergo these reactions is very varied. Some examples are given below.

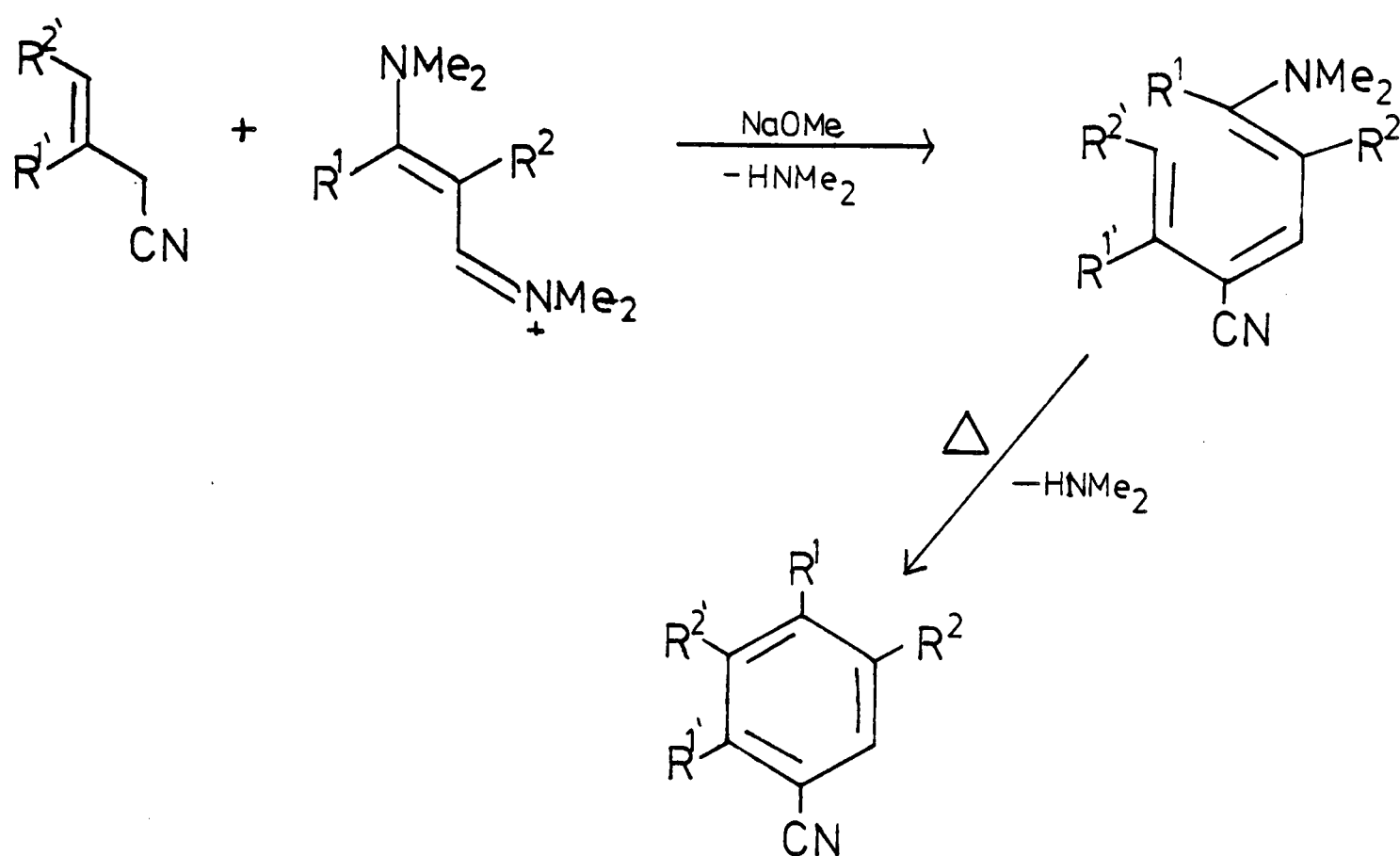
Generally, benzene ring formation involves the use of vinamidinium salts (18) and stabilised carbanions often generated from diethylglutaconate or glutaconitrile (20) and from substituted allyl cyanides⁵⁵ (crotonitriles) (21) (Scheme 35).



Y = CO₂Et, diethylglutaconate
Y = CN, glutaconitrile⁵⁴

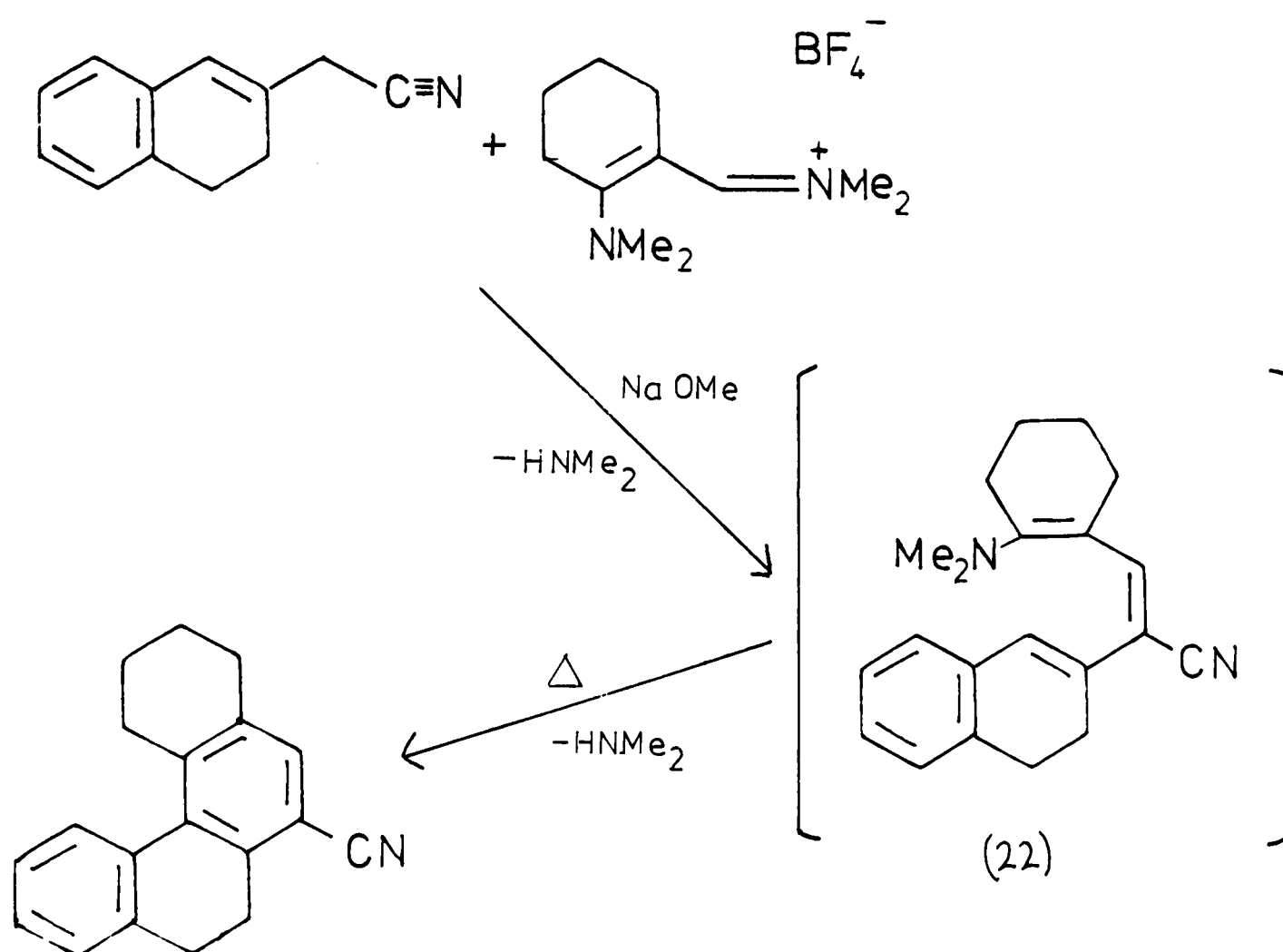


The wide range of vinamidinium salts can also be extended to mono- and bicyclic derivatives (prepared from the corresponding ketone⁵⁶). A surprising range of combinations is therefore possible.



Scheme 35

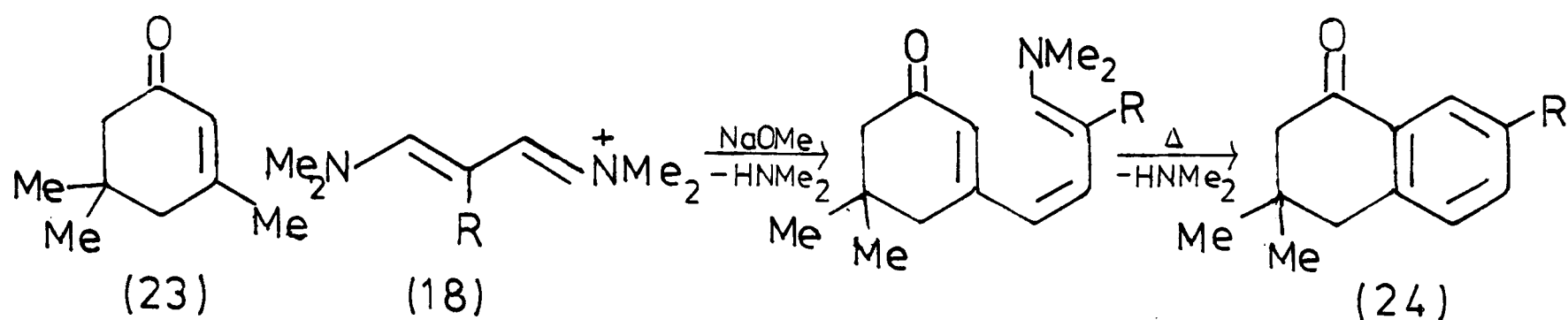
The synthesis of more complex hydrocarbons can be approached simply by the combination of two cyclic components, as shown in Scheme 36.



Scheme 36

The intermediate hexatriene (22) can only cyclise from the less favourable *Z*-form, relative to the dimethylamino group, however, the reaction still proceeds in good yield.

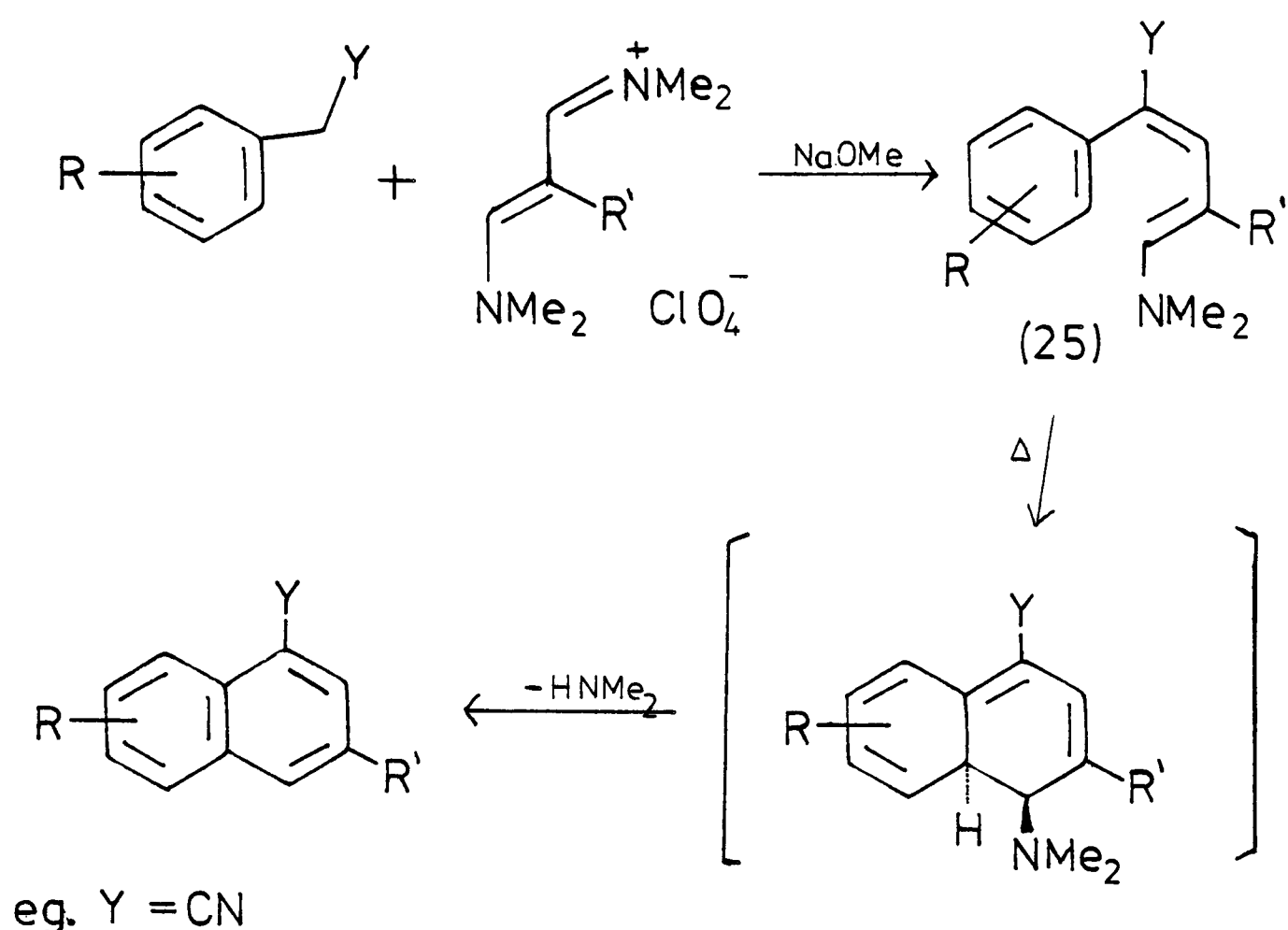
3,5,5-Trimethylcyclohex-2-enone (23) readily condenses with vinamidinium salts (18) in the presence of sodium methoxide and, on heating, cyclises to give 3,3-dimethyl-1-tetralones (24), with loss of dimethylamine.



Scheme 37

Perhaps the most versatile application of the electrocyclic ring closure elimination method is the benzannelation reaction. The ready availability of the starting compounds and, in general, the high yields, make this the synthesis of choice for many specifically substituted compounds.

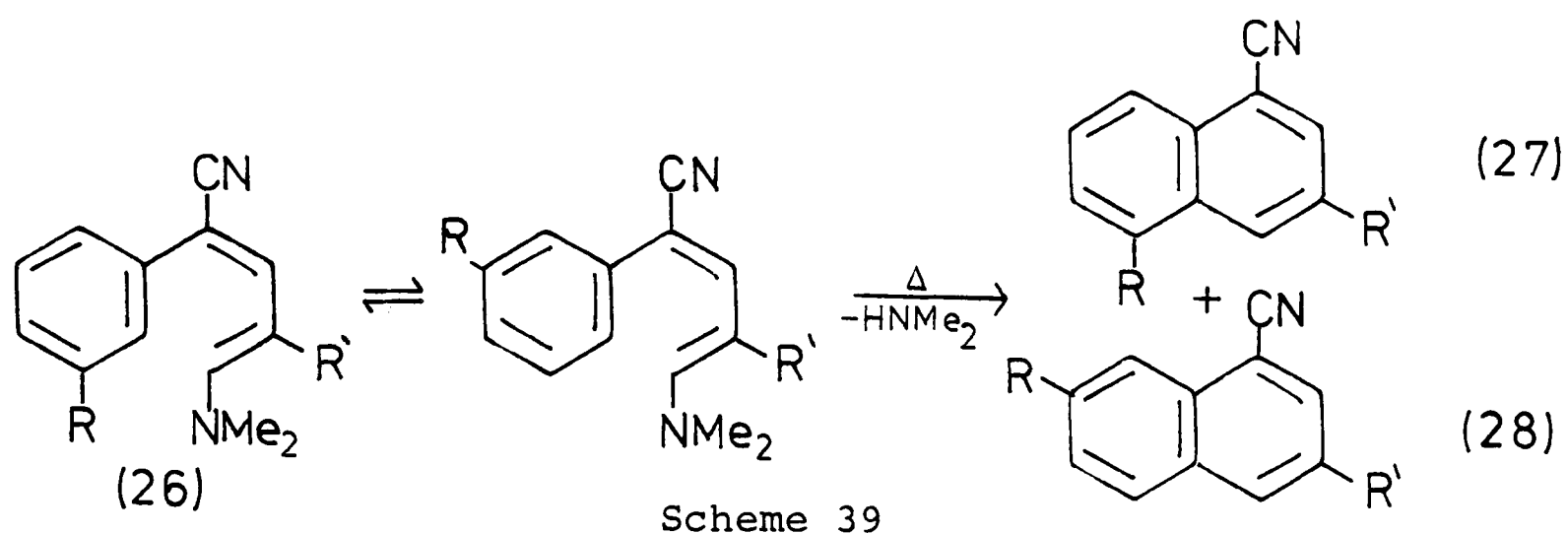
These aminohexatrienes, in which one double bond is part of an aromatic system, have a greater activation energy for cyclisation, than comparable open chain aminohexatrienes. This is associated with the loss of some aromatic resonance in the connected aromatic ring system (Scheme 38).



Scheme 38

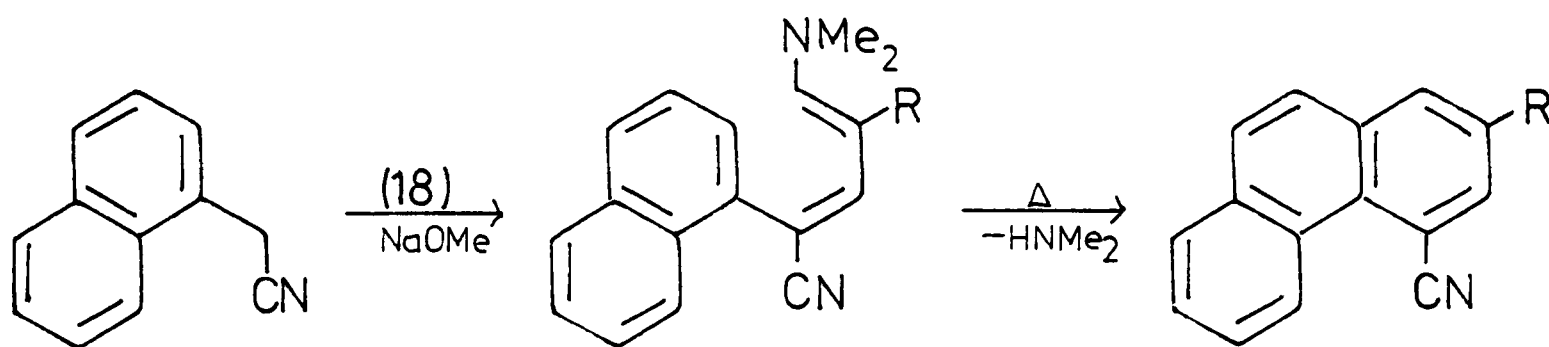
There are a large number of benzene derivatives with an active methylene which are suitable for condensation with vinamidinium salts eg. desoxybenzoin (activated by carbonyl), benzylphenylsulphones (activated by sulphonyl), esters of phenylacetic acids, and best suited, the phenylacetonitriles (activated by cyano) to give arylaminobutadienes (25) which can be cyclised to naphthalenes. However, on steric grounds, only arylaminobutadienes (25) generated from vinamidinium salts derived from malondialdehydes, can be cyclised successfully.

If a *meta*-substituted phenylacetonitrile is used, then the arylaminobutadiene intermediate (26) may ring close in two directions, giving rise to a mixture of 5- and 7-substituted 1-naphthonitrile as shown in Scheme 39.



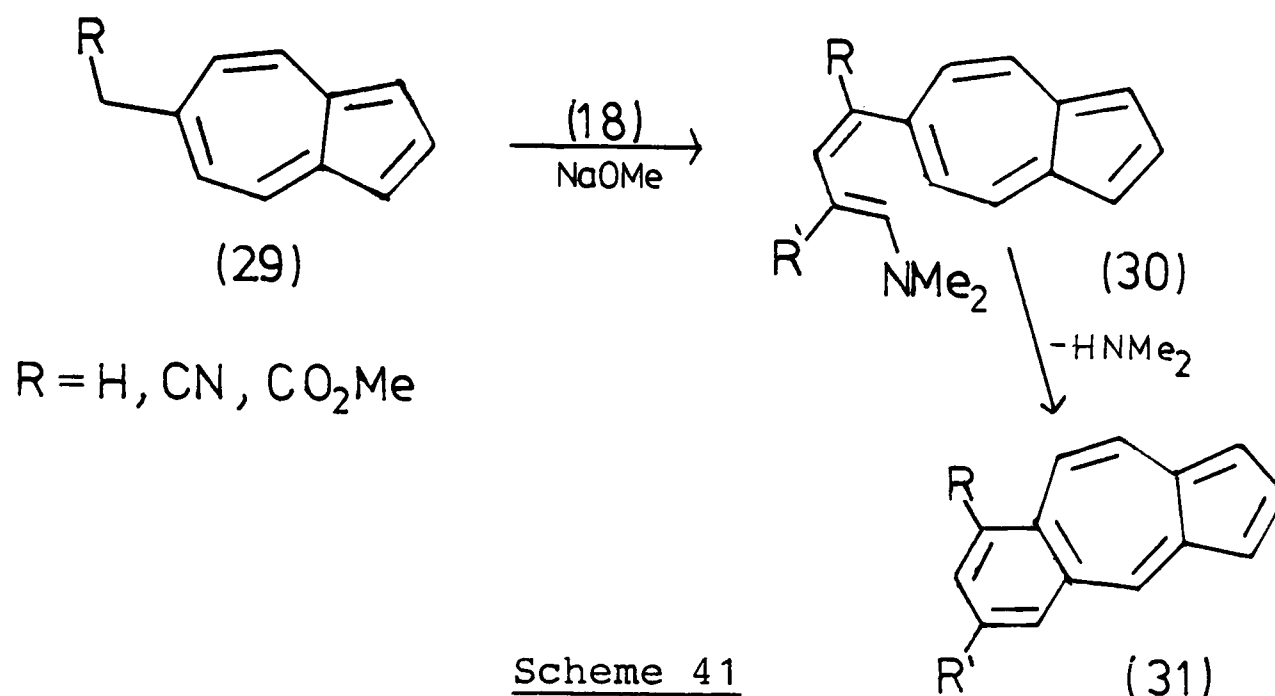
The ratio of the two isomers formed depends mainly on the nature of the substituent R, and to a minor extent on the substituent R'. Small R substituents (eg. CN) favour the formation of the 5-isomers (27) whereas bulky substituents (eg. CF₃) favour the 7-isomers (28).

The easily available naphthalene acetonitriles are suitable starting components for the benzannulation of naphthalene,⁵⁷ giving phenanthrenes (Scheme 40). Similarly,



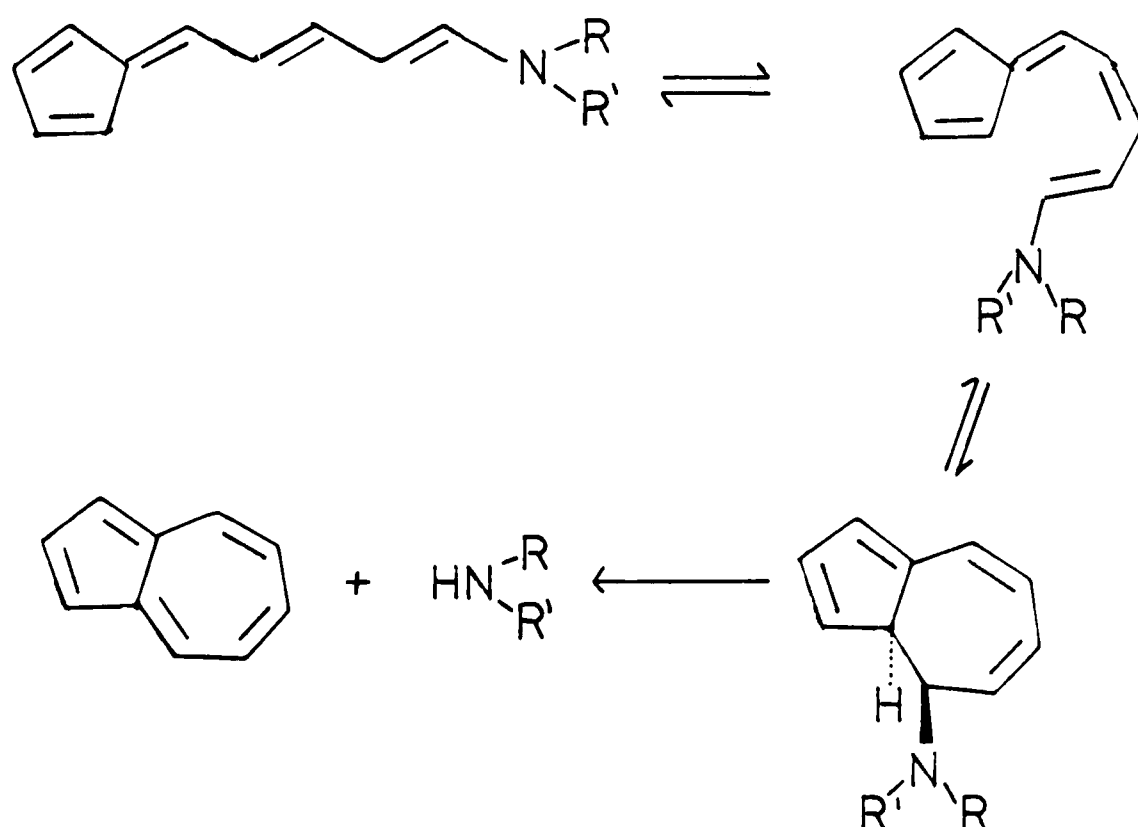
three tetracyclic systems, triphenylene, benzphenanthrene and chrysene, can be derived by angular benzannulation of phenanthrene.

Various azulenes and azulenoids can also be prepared by benzannulation (Scheme 41). Methyl groups at positions



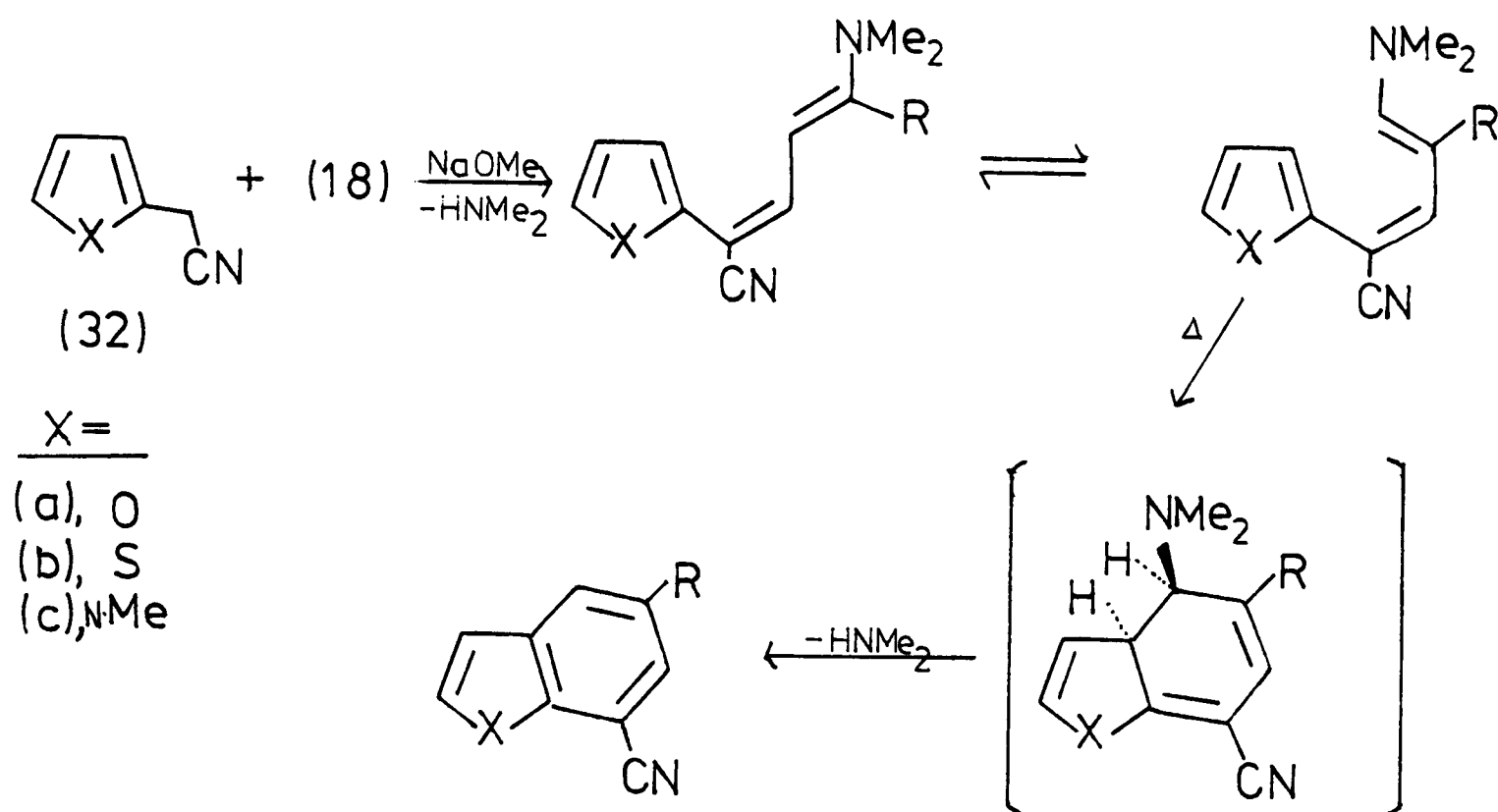
4,6 or 8 of azulene are just acidic enough to undergo condensations with vinamidinium salts (18) and their vinylogues (19), in the presence of sodium methoxide. On heating, the azulene dienamine (30) loses dimethylamine to form the benzazulene (31). However, the reaction does not run to completion and unconverted azulene (29) can be recovered.⁵⁸

It is interesting that this electrocyclic ring closure with elimination reaction can be applied to the synthesis of the azulene ring system as in the classic Ziegler-Hafner synthesis⁵⁹ (Scheme 42). This involves a thermal 10 π electron



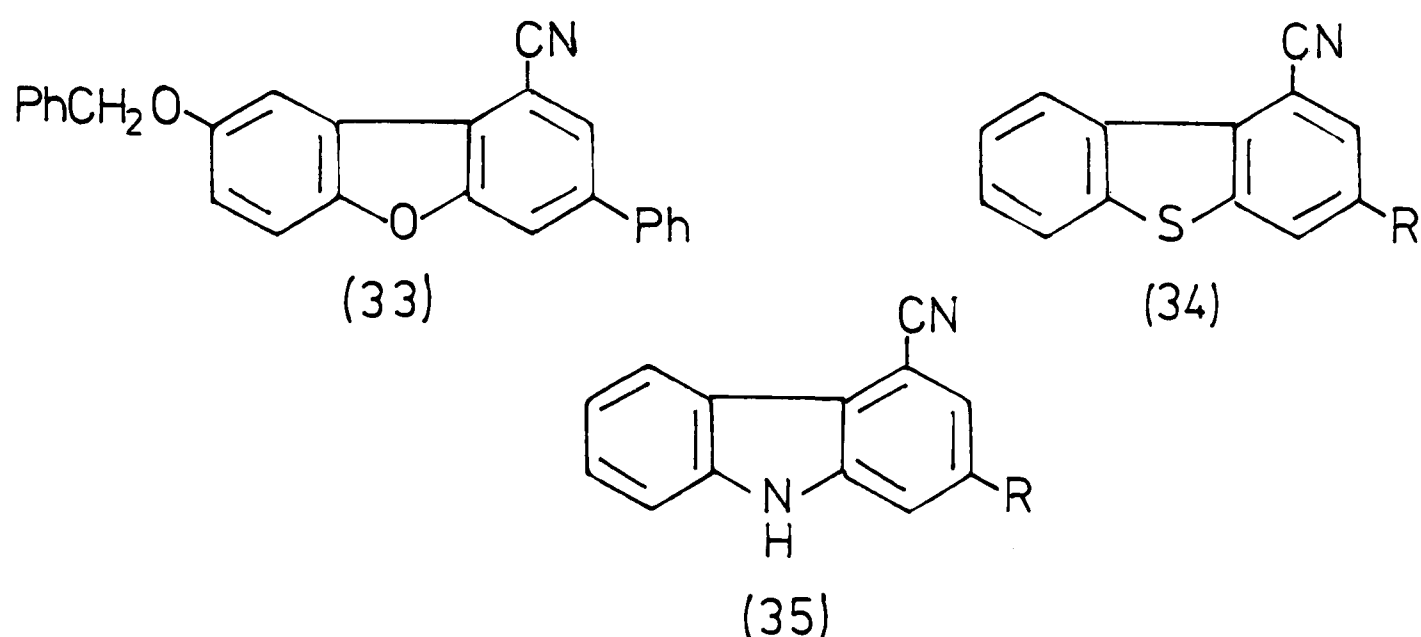
electrocyclic ring closure with elimination of dialkylamine.

Benzannelation can also be used for the synthesis of heterocycles.

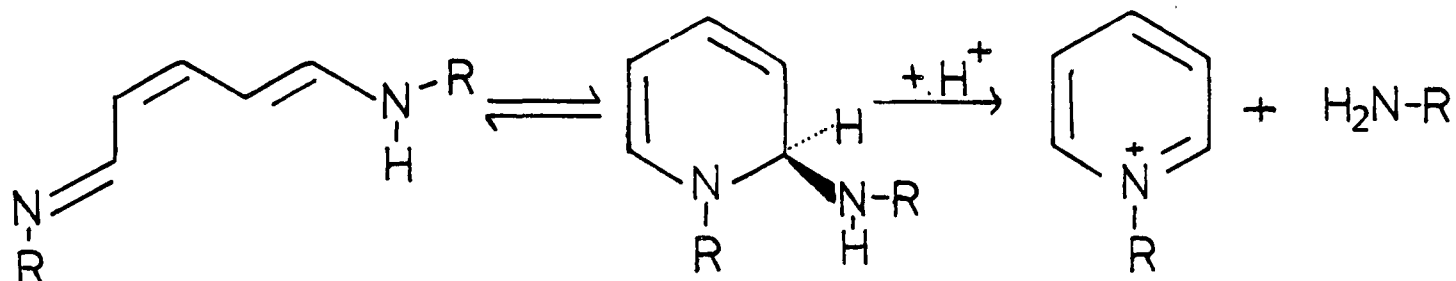


Scheme 43

Scheme 43 shows how the 2-acetonitriles of furan (32a), thiophen (32b) and N-methylpyrrole (32c) are readily transformed to their corresponding benzoderivatives. For the synthesis of dibenzofuran (33), dibenzothiophenes (34) and carbazoles (35) by benzannelation, in the same manner, the 3-acetonitrile of benzo(b)furan, benzo(b)thiophen and of indole are used.

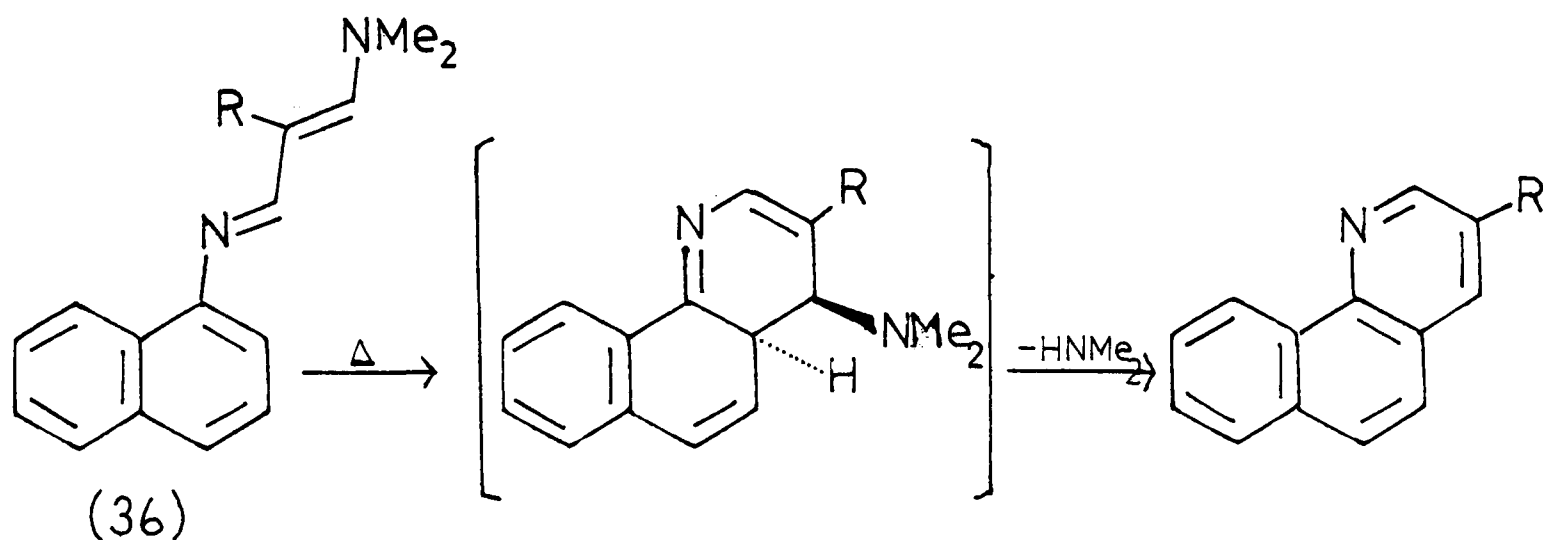


Heterocycles can also be synthesised by the electrocyclic ring closure of azohexatrienes, with elimination.⁶⁰ For example, pyridines can be synthesised this way as shown in Scheme 44.



Scheme 44

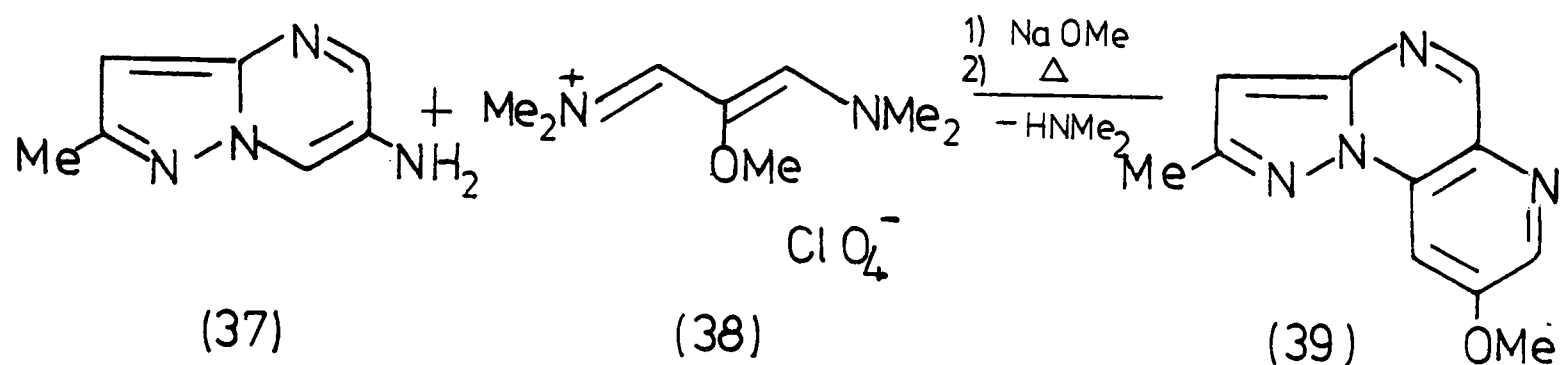
More complex pyridines can be obtained in the same manner, as can quinolines, benzoquinolines etc. Studies of the mechanism of quinoline formation under gas phase pyrolysis are reported at a later stage of this thesis.⁶¹



Scheme 45

The thermolysis of (36) opens a general way for pyridoannulation of structurally appropriate aromatic and heteroaromatic compounds.

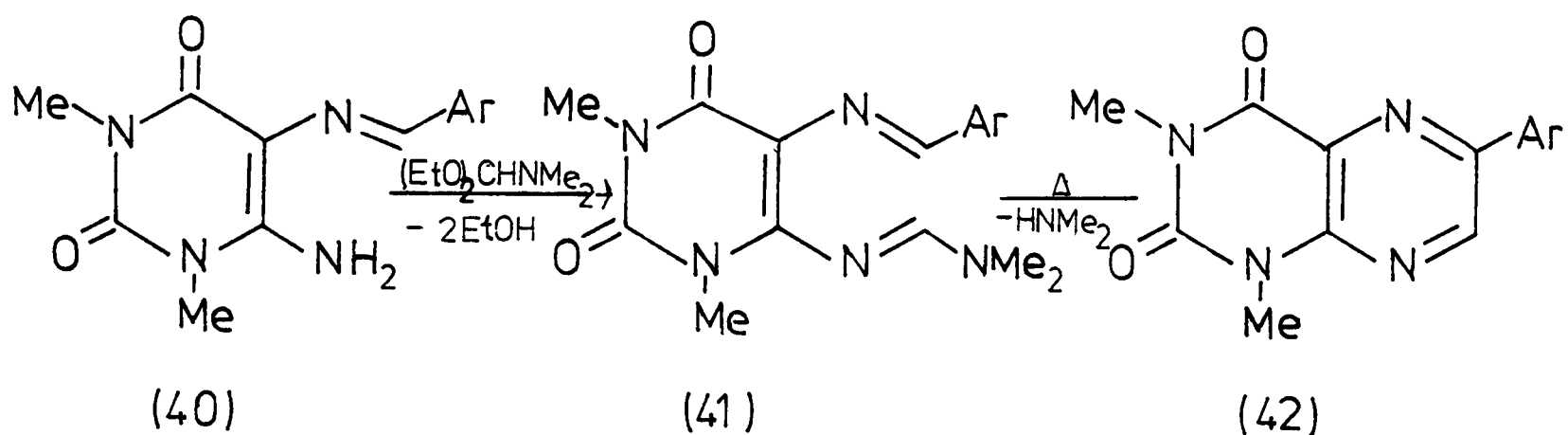
N-Bridged heterocycles are made in a similar way. For example, application of pyridoannulation to the amino derivative



Scheme 46

(37) with (38) gives the fused pyrimidine (39).

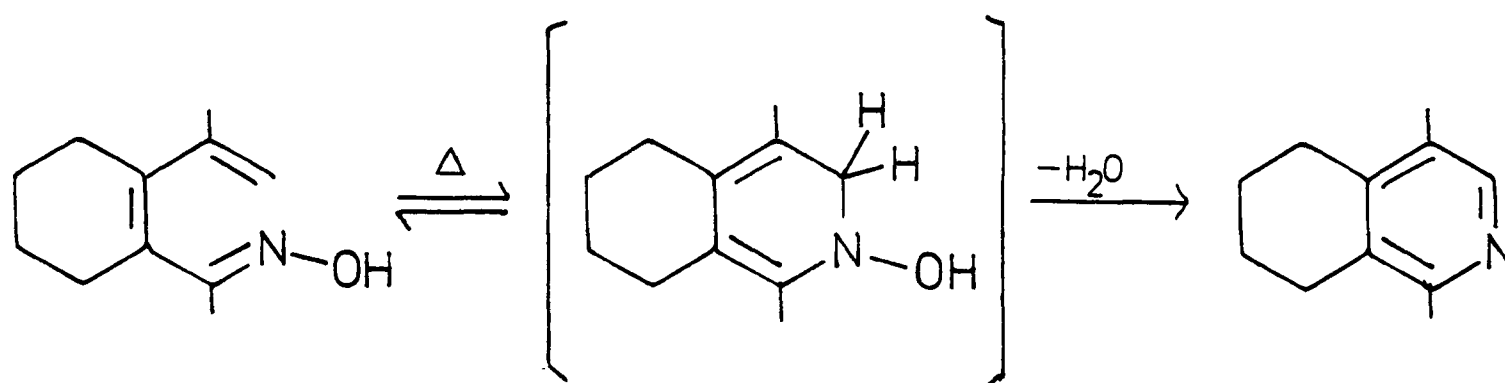
There are many other reactions to be found which are best explained by an electrocyclic process with subsequent elimination. They generally take place under milder conditions, presumably due to the geometry of the triene being correct for cyclisation.



Scheme 47

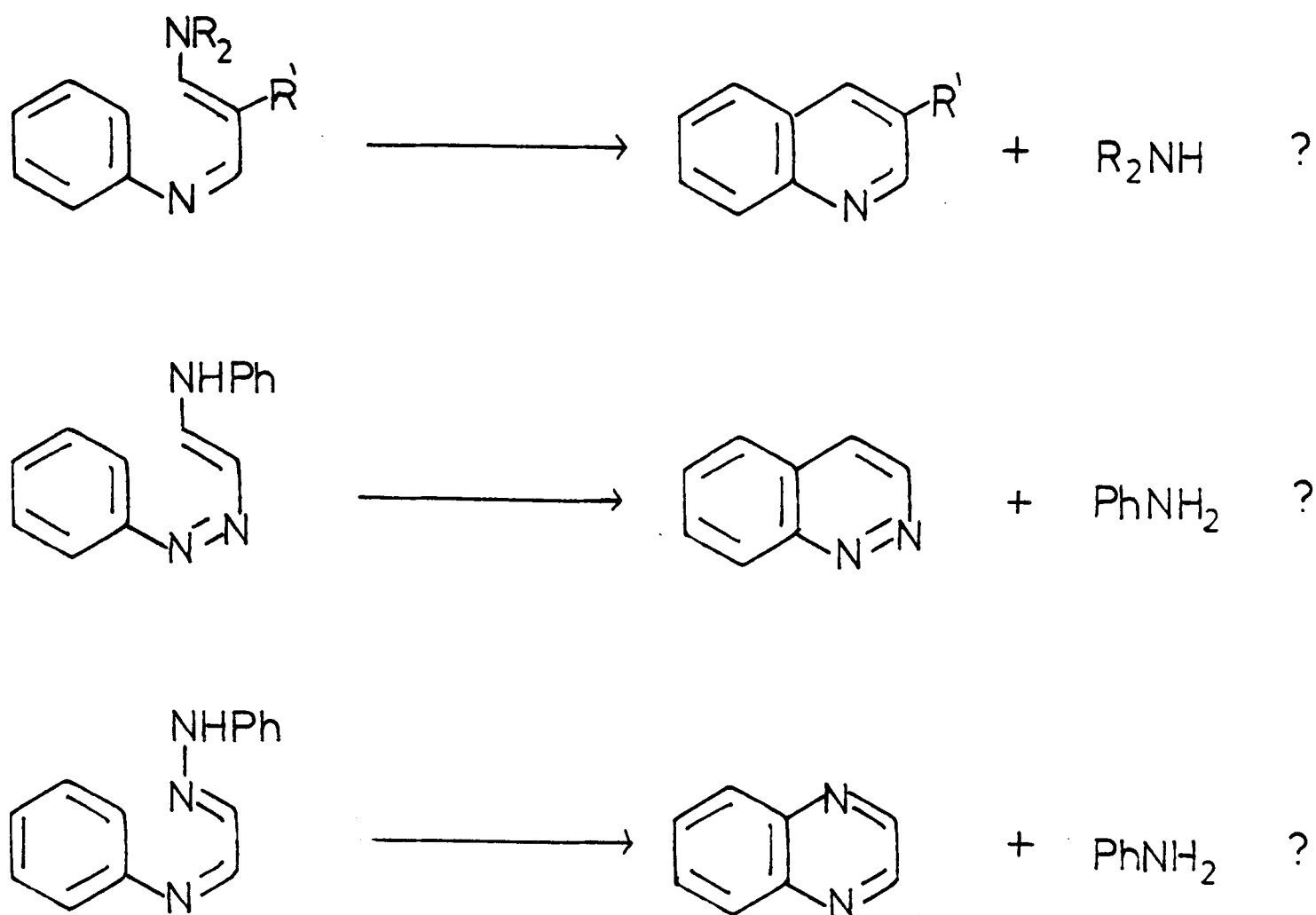
The aminouracil derivative (40) condenses with dimethylformamide diethylacetal to the dimethylaminomethyleneamino compound (41), the thermolysis of which leads to the pyrimido (4,5-b) pyrazine (42).⁶²

Scheme 48 shows how diene-one oximes of right configuration are able to form pyridines by loss of water.⁶³

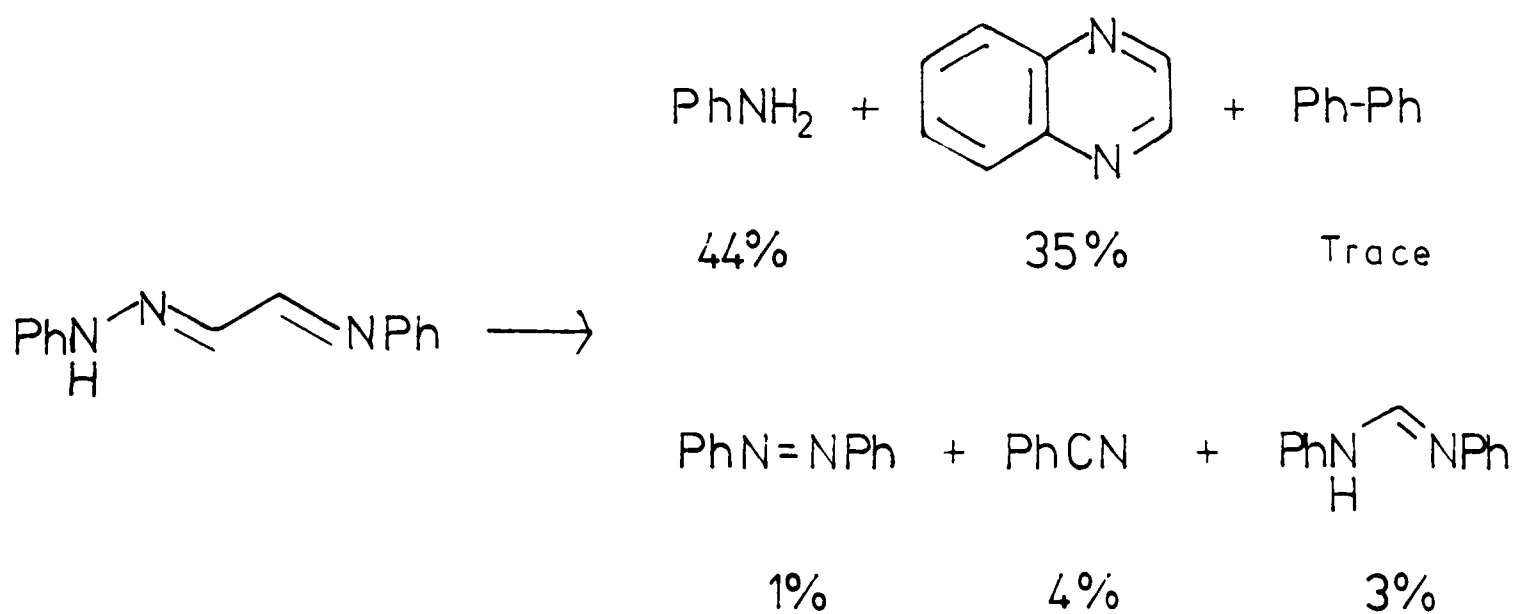
Scheme 48

3. Ring Closure with Elimination in the Gas Phase

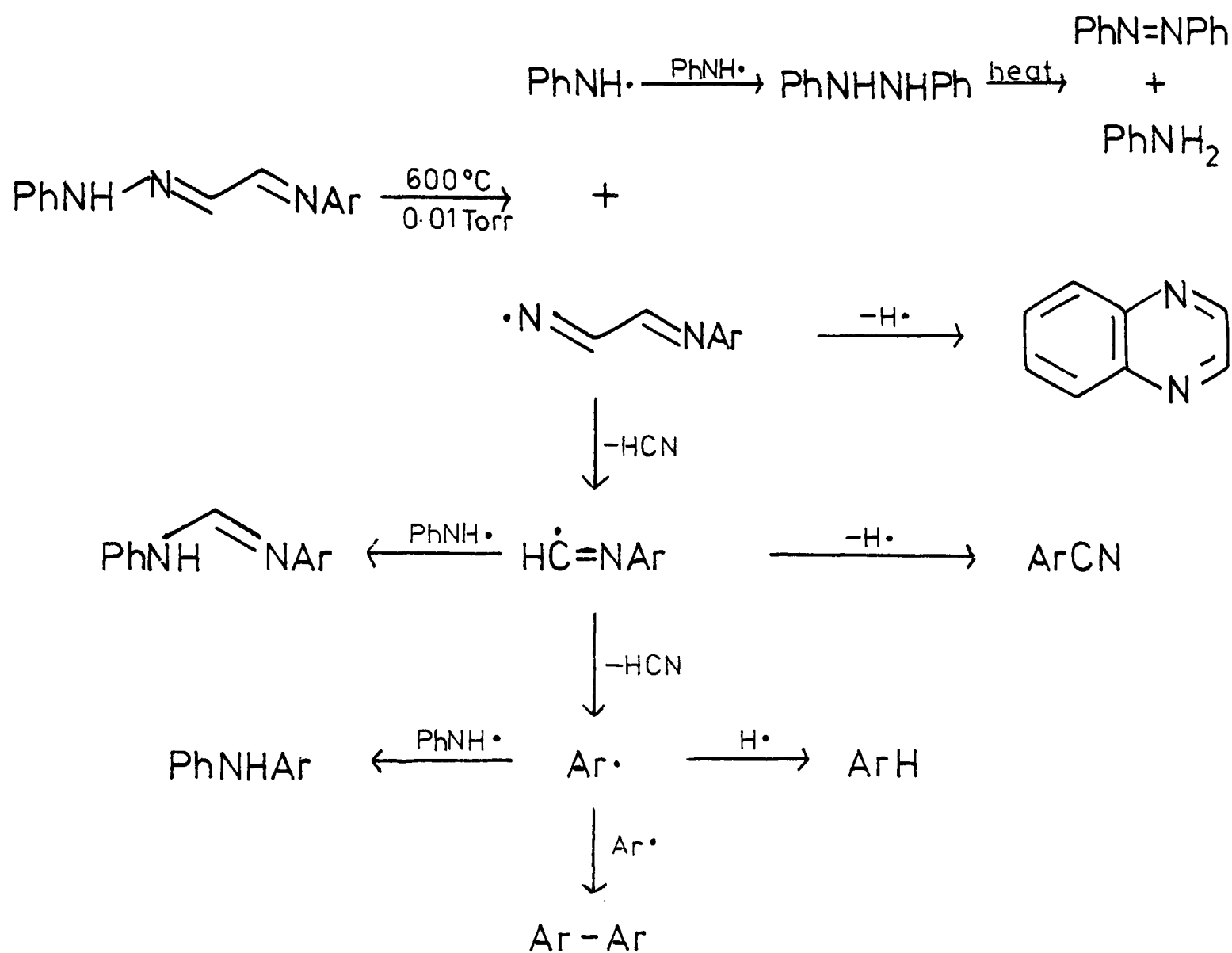
As discussed previously, Jutz and his co-workers have elegantly exploited the thermal cyclisation of 1-aryl-1,5-diazapentadienes to give quinolines⁵² and have shown that these are concerted electrocyclic reactions. Similarly, 1,5-diaryl-1,2,5-triazapentadienes might be expected to cyclise either to give cinnolines or quinoxalines depending on the tautomeric form of the base (Scheme 49).

Scheme 49

It was found that quinoxaline was the only heterocyclic base present after flash vacuum pyrolysis.⁶⁴ No cinnoline was present.

Scheme 50

In addition to quinoxaline and aniline, a number of minor products were identified as shown in Scheme 50. These were clearly unexpected on the basis of a concerted reaction and so were investigated by two cross-over experiments (pyrolysis of the *p*-tolyl derivative and a co-pyrolysis of the 1,5-diphenyl and 1,5-di-*p*-tolyl derivative) which confirmed that a radical pathway was taking place. The proposed mechanism in Scheme 51 is able to account for the products obtained.

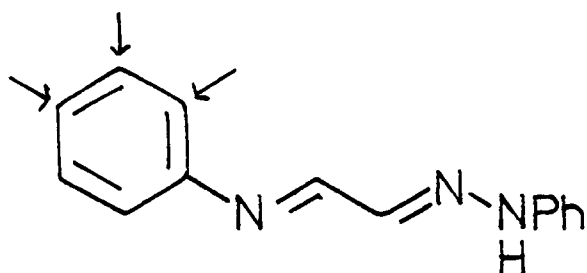


Scheme 51

The presence of the iminyl radical offers an alternative to the electrocyclic mechanism, for ring closure to the quinoxaline. Iminyls are known to effect intramolecular aromatic substitution in solution, and indeed cyclisation of

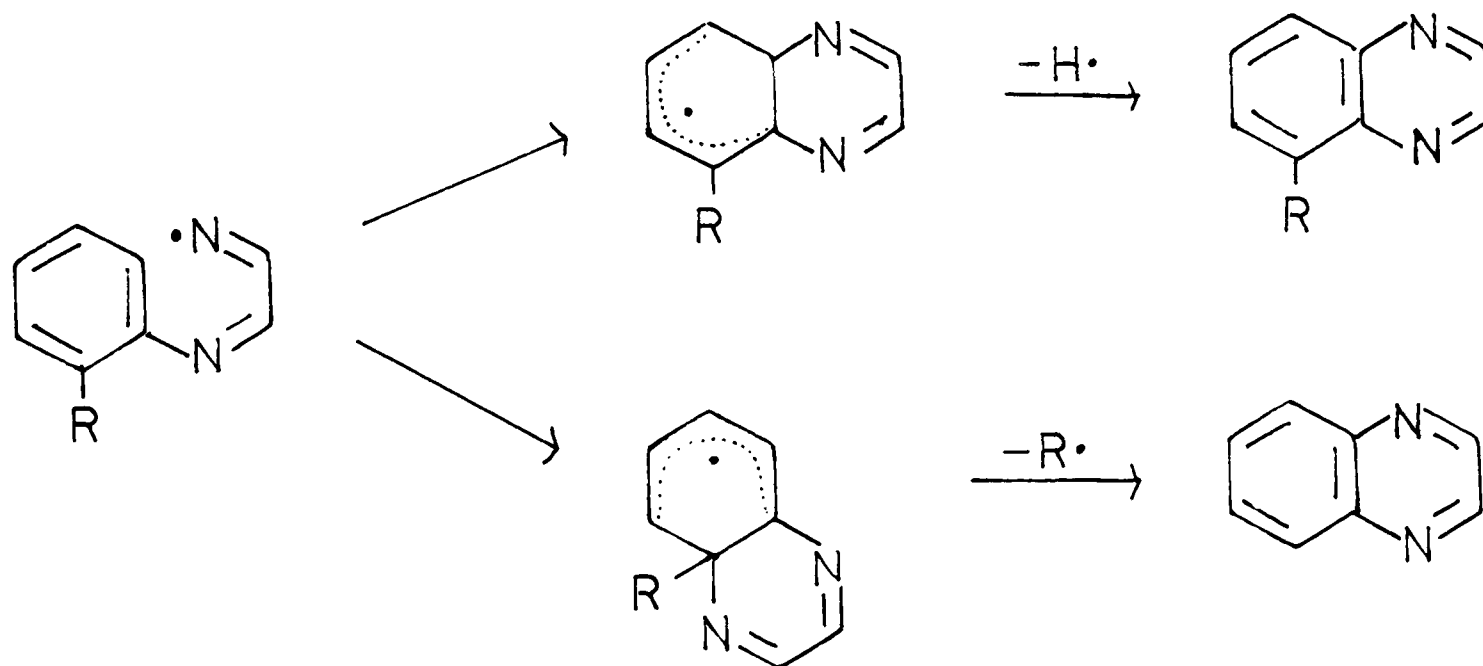
vinyliminyls to quinolines has been observed in favourable cases.⁶⁵

The effect of substituents in the 5-aryl ring on the radical cyclisation reaction have been studied.⁶⁶



As expected 6-substituted quinoxalines were obtained exclusively from the *p*-substituted derivatives.

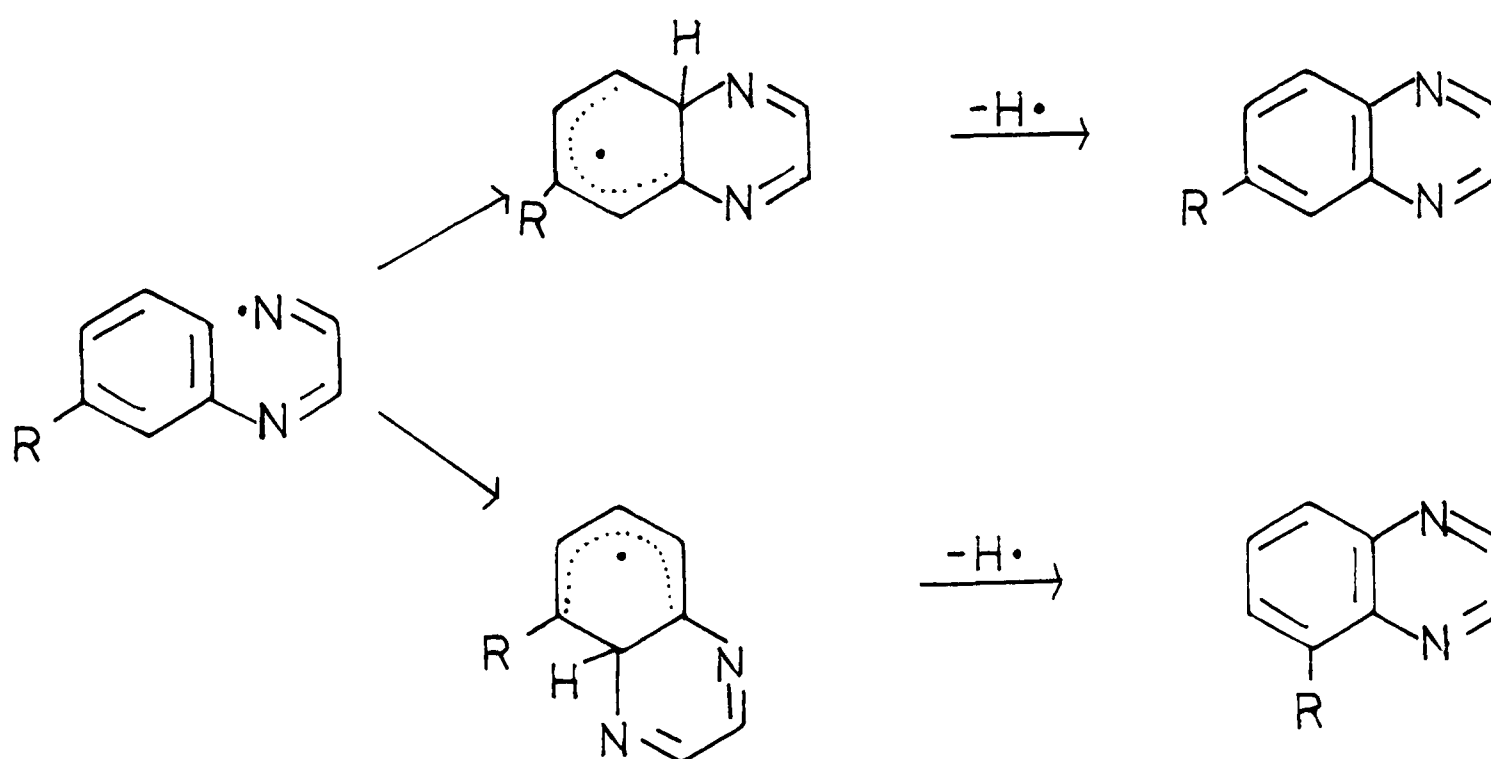
Pyrolysis of the *o*-substituted derivatives was of particular interest from a synthetic point of view since the expected 5-substituted quinoxalines are normally obtained from 3-substituted *o*-phenylenediamines, whose preparation is often tedious.⁶⁷ The appropriate quinoxaline was indeed generated by pyrolysis of the triazapentadiene but the yield was low and quinoxaline itself was a major contaminant (Scheme 52).



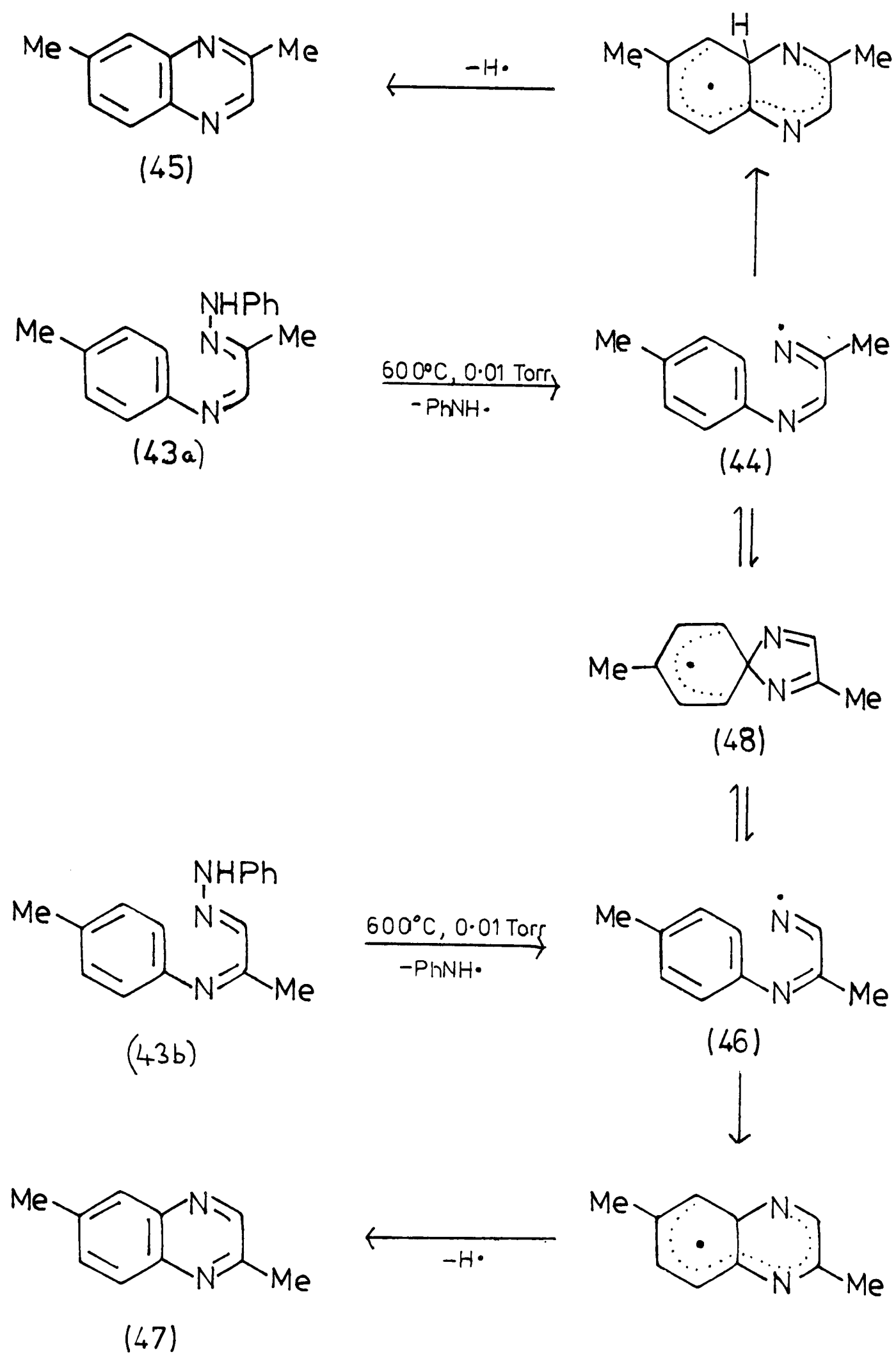
Scheme 52

The two products arise by competitive attack of the iminyl on the two positions *ortho* to the radical side chain, followed by ejection of the ring junction substituent. It is perhaps surprising that the parent quinoxaline is not the major product in all cases (due to high heat of formation of the hydrogen atom), though steric requirements for this *ipso* attack are probably unfavourable.

Mixtures of quinoxalines were also obtained from the pyrolyses of the *m*-substituted compounds again due to attack at the two positions *ortho* to the side chain and led to 5- and 6-substituted quinoxalines respectively (Scheme 53). The ratio of the products depends strongly on the substituent - the 5-isomer is dominant for compounds with *m*-alkyl substituents, while the 6-isomer is the major product for those with electron-withdrawing or electron-donating *m*-substituents. The dependence is distinct from that found by Jutz⁵² for the concerted electrocyclic process.



Scheme 53



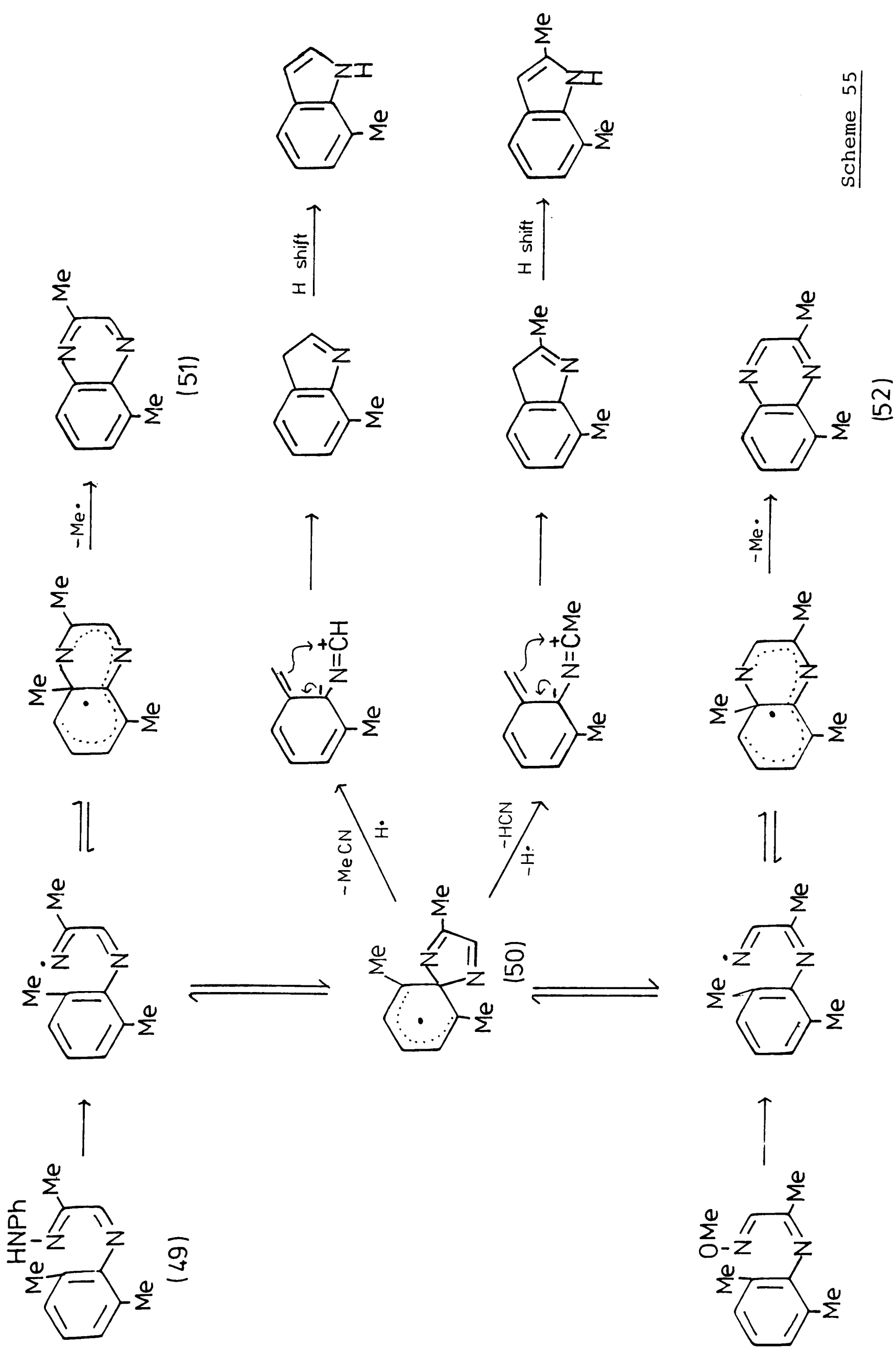
Scheme 54

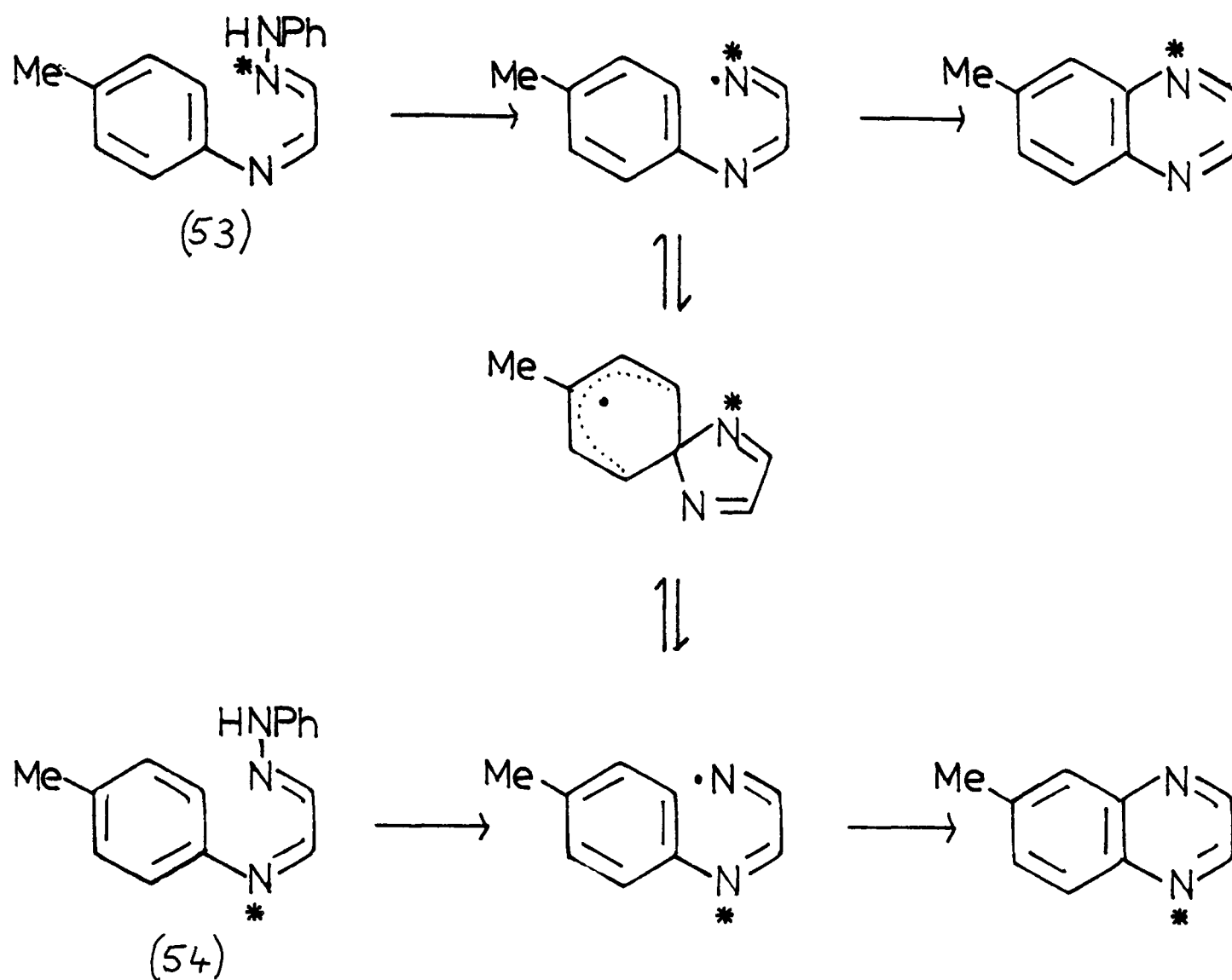
Further experiments have clarified the mechanism of the cyclisation step.⁶⁸ These experiments include the first examples of degenerate rearrangement of iminyls.

Generation of the iminyl (44) by pyrolysis of the hydrazone (43a) was expected to lead exclusively to the quinoxaline (45) by direct cyclisation as shown in Scheme 54. In fact, two isomeric quinoxalines, (45) and (47) are formed. Similarly, (43b) leads to the same products, but in different ratios. This suggests that the iminyls (44) and (46) can interconvert *via* the spirodienyl radical (48), but that this process competes with direct attack at the *ortho* position.

In order to evaluate quantitatively the contribution of the two mechanisms, it was necessary to assume that the migration tendencies of the two nitrogen atoms of the spirodienyl radical (48) were equal,⁶⁹ however this has been shown to be invalid for the related spirodienyl radical (50).⁷⁰

The major quinoxaline formed from the pyrolysis of (49) (as shown in Scheme 55) was found to be (52). If the nitrogen atoms in the spirodienyl radicals had equal migration tendencies, the amount of quinoxaline (52) could at most only equal (51) (based on the total involvement of the spirodienyl radical). However, the major product from the dimethyl compound (49) is actually 7-methylindole formed by nitrile cleavage from the spirodienyl (Scheme 55).





Scheme 56

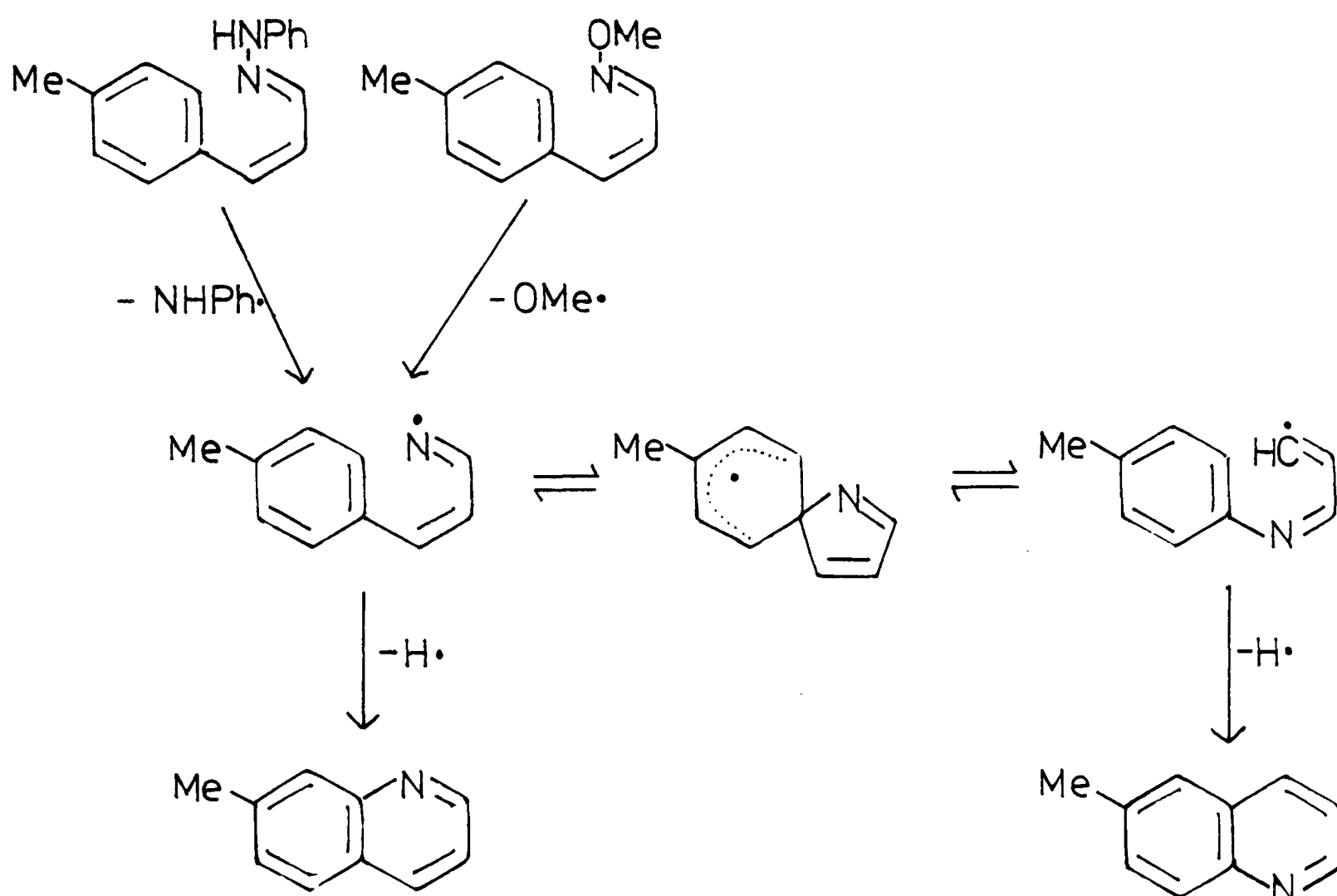
The role of the spirodienyl in the cyclisation reaction was investigated in more detail by ^{15}N labelling studies.⁷¹ The ^{15}N n.m.r. spectrum of the pyrolysate of compound (53) showed two peaks as expected for 6-methylquinoxaline. Therefore possible interconversion *via* a benzvalene type intermediate⁷² can be excluded, since this route does not interchange the position of the nitrogen atoms. The major peak corresponds to N(4) which confirms earlier speculation that direct cyclisation might compete with equilibration *via* the spirodienyl radical. Pyrolysis of (54) also gave 6-methylquinoxaline as expected, but this time the major peak was due to N(1).

Quantification of the reaction path of direct and

spirodienyl cyclisations (allowed due to the high symmetry of the system) gives a spirodienyl component of 88% with a 12% leakage to product by direct cyclisation.

To summarise, the gas phase pyrolysis of 5-aryl-1,2,5-triazapentadienes leads to quinoxalines, but by an iminyl radical mechanism.⁶⁴ The reactions proceed under relatively mild flash vacuum pyrolysis conditions (600-650°C), but the yield of quinoxalines is moderate and many by-products are formed. Nevertheless this procedure has been extended to other ring systems, with results of some preparative significance.

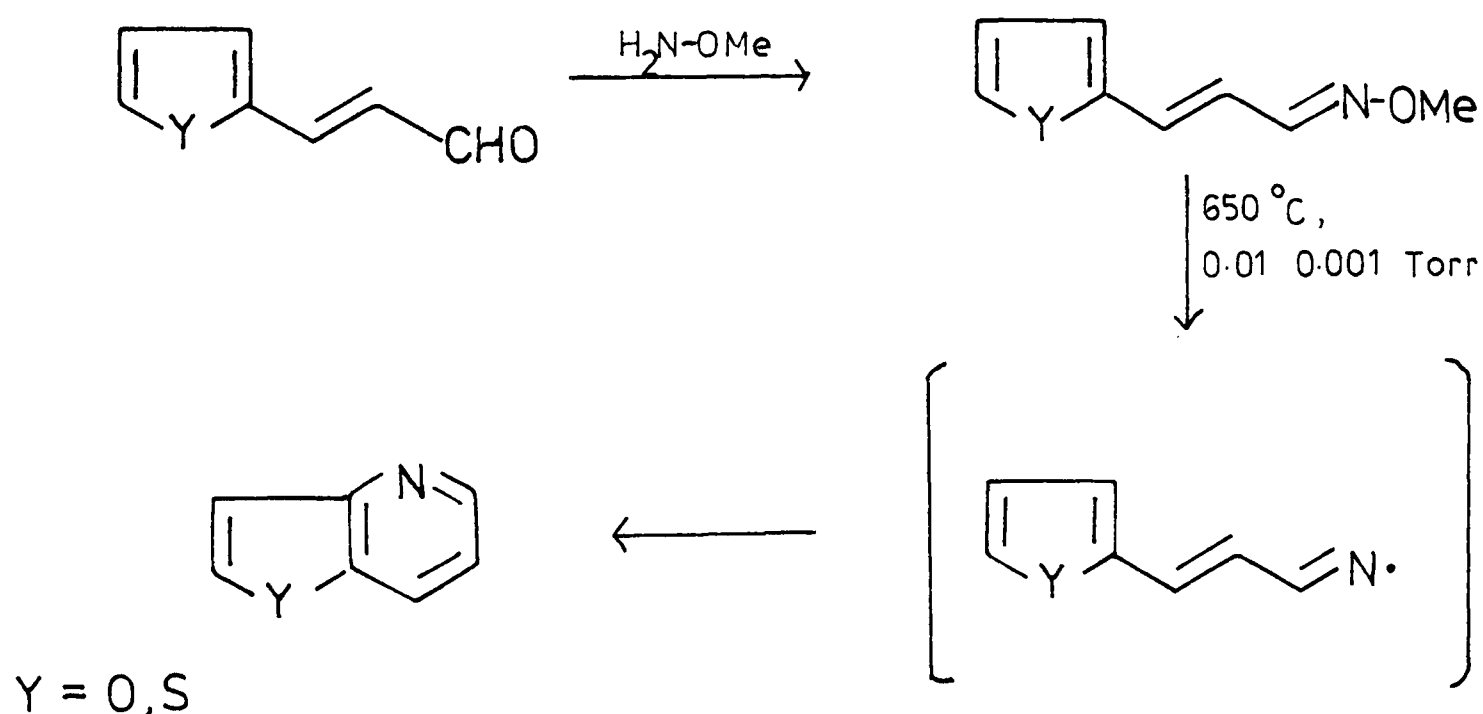
Flash vacuum pyrolysis of cinnamaldehyde phenylhydrazone derivatives has also been reported,⁷³ with approximately equal quantities of cinnamonitriles and quinolines being found (Scheme 57).



Scheme 57

A *p*-substituted cinnamaldehyde derivative gives the appropriate 7-substituted quinoline in high isomeric purity. This was also of particular interest in a mechanistic context since cyclisation *via* the spirodienyl mechanism might result in a mixture of 6- and 7-methylquinolines. This suggests that either direct cyclisation occurs, or that C-N migration from the spirodienyl radical is favoured over C-C migration. Formation of related spirodienyl radicals in solution does indeed result in products derived from C-N migration⁷⁴ though this has still to be proved to be the case in the gas phase.

A new, simple route to furo and thieno [3,2-*b*]pyridines has been reported⁷⁵ (Scheme 58).



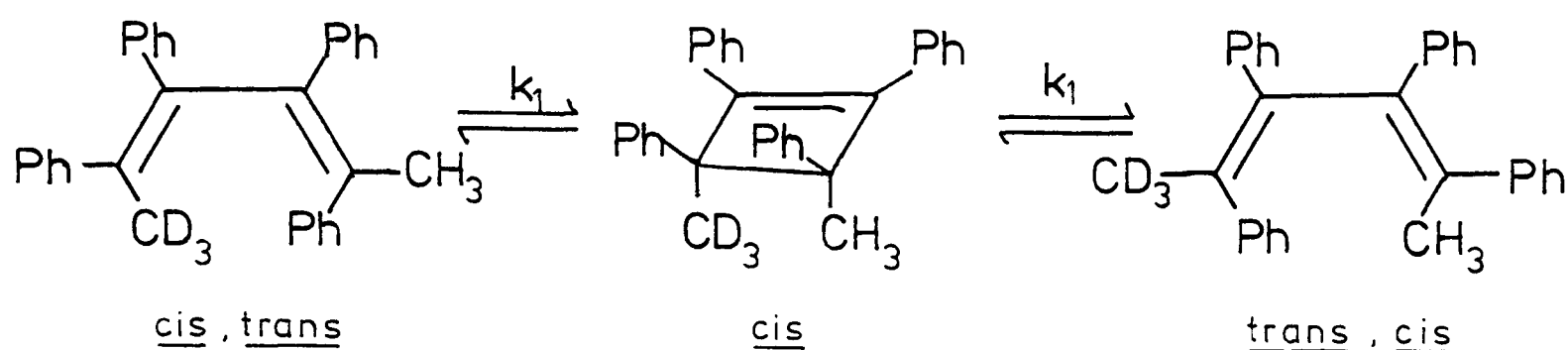
Scheme 58

The reactions are based on the one-step generation of the pyridine ring by gas phase cyclisation of conjugated iminyl radicals.

III PYROLYTIC AND ELECTROCYCLIC REACTIONS

1. Cyclobutenes and Butadienes

There is only limited data⁷⁶ on the thermal electrocyclic ring closure of dienes to cyclobutenes because butadiene is normally the more stable. However a series of substituted dienes, in which steric constraints lead to facile cyclisation, have been reported.^{77,78}

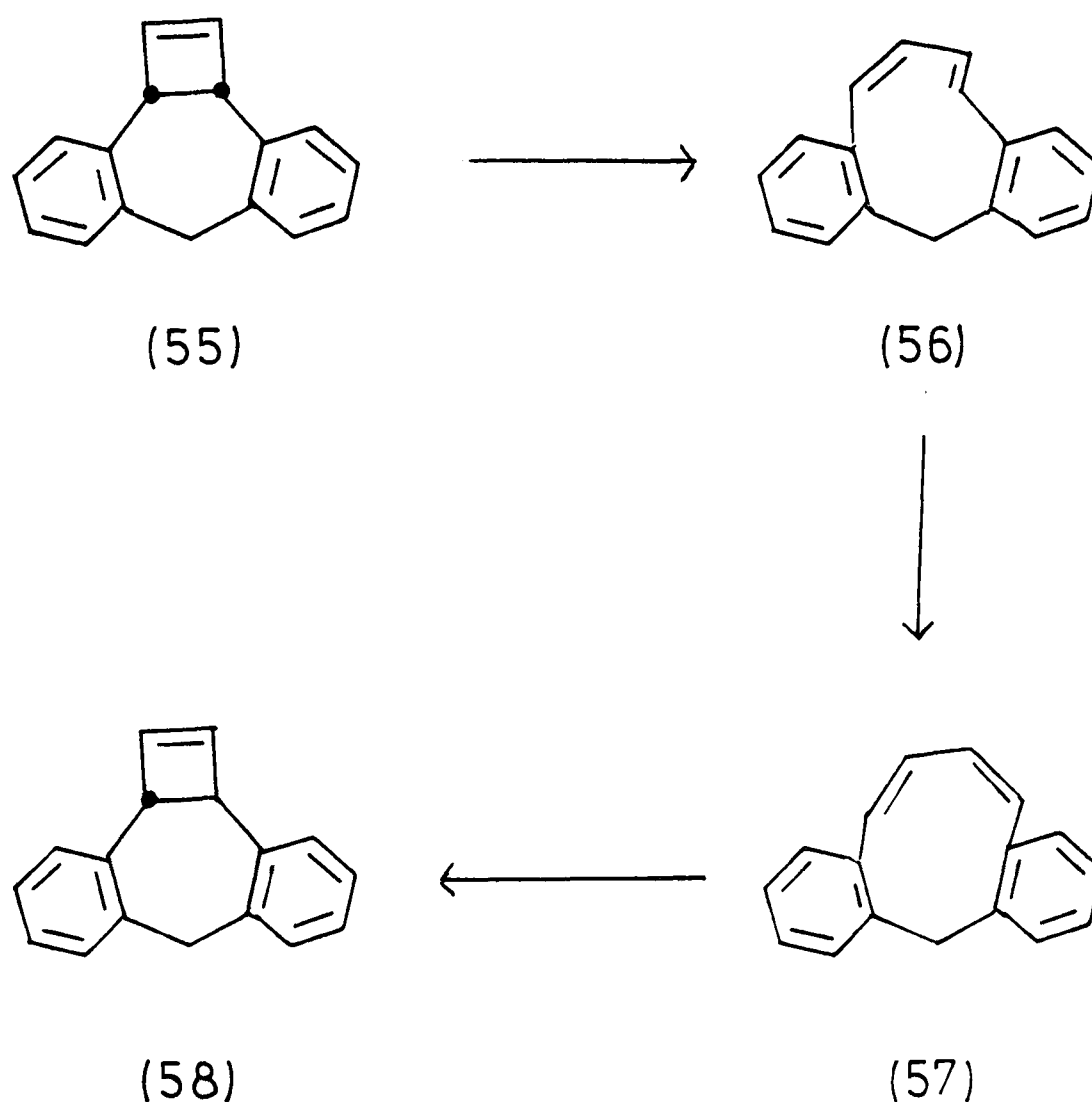


Scheme 59

Reversibility in a cyclobutene-butadiene electrocyclic reaction can be demonstrated by obtaining the same equilibrium distribution of diene and cyclobutene starting with either component.⁷⁷ Alternatively, in the typical case where the equilibrium concentration of cyclobutene is unobservable, reversibility can be inferred if thermal geometrical isomerisation of the dienes occurs only between conrotatory isomers to give an equilibrium distribution which is demonstrably different from the normal thermodynamic distribution of isomeric dienes⁷⁸ (Scheme 59)

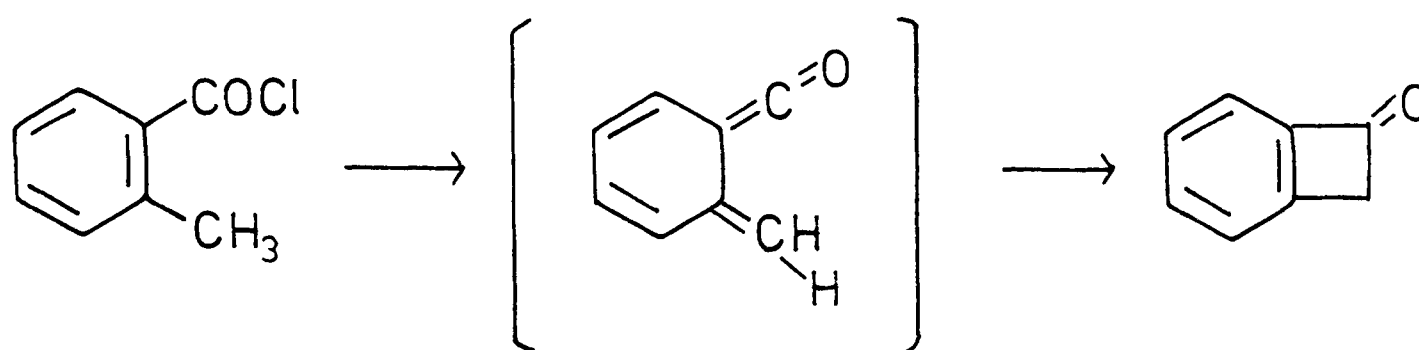
There is only limited literature on the flash vacuum pyrolysis of dienes leading to cyclobutenes by electrocyclic ring closure, although there are many examples of the ring opening of cyclobutene rings, fused to further rings, in the

gas phase.^{79,80,81} However, the preferred conrotatory mode of opening may be disfavoured by the ring-size of the product, or the initial stereochemical outcome may be changed through secondary isomerisation. Willner and Rabinovitz⁸² found that pyrolysis of 2,3:5,6-dibenzobicyclo[5.2.0]non-8-ene (55) did give the primary product of conrotation, the *cis,trans*-nona-tetraene (56), but this was accompanied by the *cis,cis* compound formed by secondary isomerisation. At higher temperatures, the sole product was the *trans* fused bicyclononene (58), the product to be expected of conrotatory cyclisation of (57).



Scheme 60

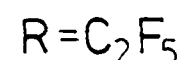
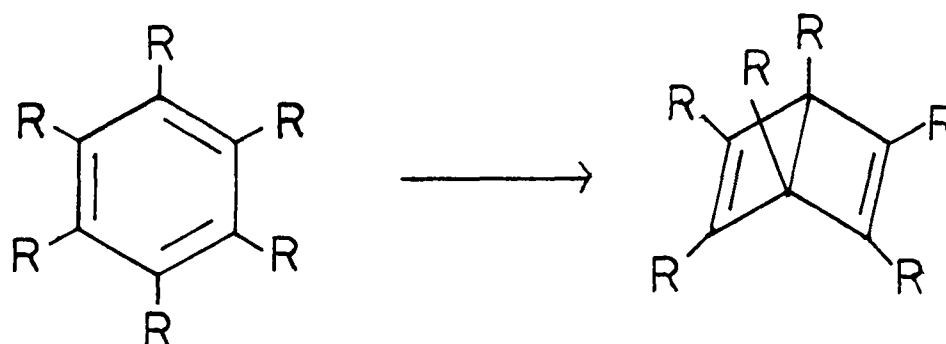
Alternatively, the formation of a benzenoid system can act as a driving force for the 4π cyclisation reactions. Gas phase pyrolysis (600°C) of 2-methylbenzoyl chloride results in the elimination of hydrogen chloride, giving an alkenylketene. This then readily undergoes thermal electrocycloisatation to give benzocyclobutenone, (Scheme 61).^{83,84}



Scheme 61

This method of preparing benzocyclobutenones competes successfully with other procedures on account of the ready accessibility of the reactants and experimental simplicity.

Another example of a 4π thermal electrocycloisatation involves the formation of Dewar benzene, using flow pyrolysis (400°C , 1 Torr), from the corresponding aromatic compound (Scheme 62).⁸⁵

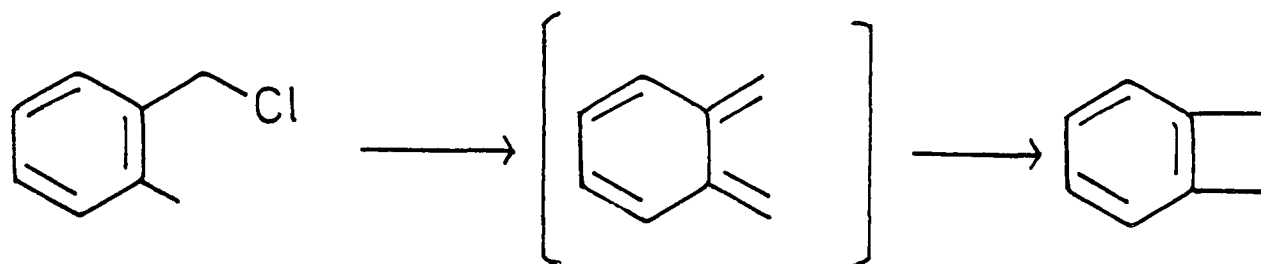


Scheme 62

In this case, the driving force is presumably relief of steric strain (or crowding in the starting material).

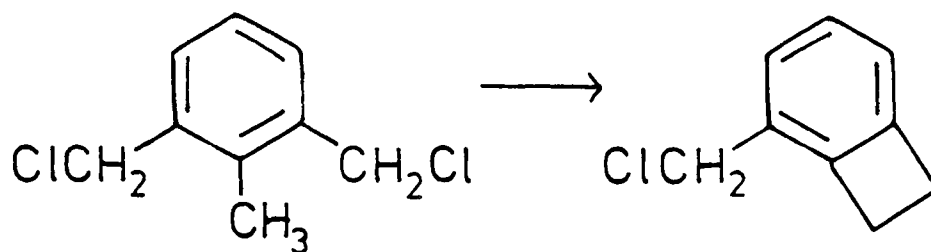
Benzocyclobutenes are similarly obtainable through flash

pyrolysis of benzylchlorides, (Scheme 63).^{86,87}



Scheme 63

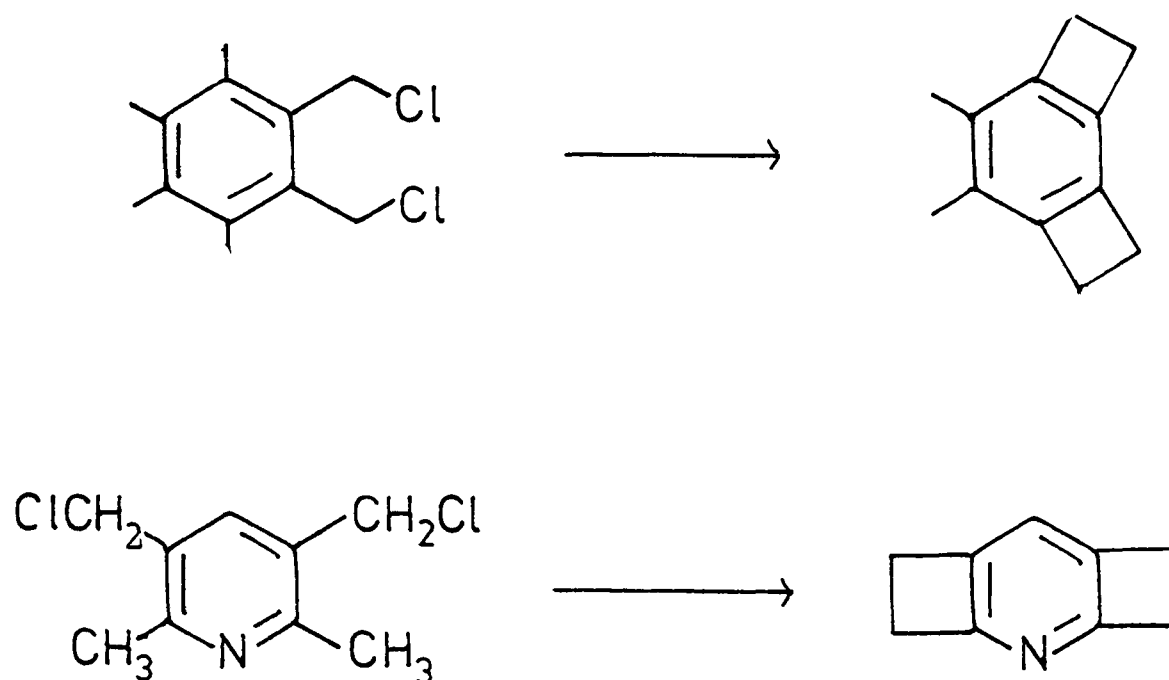
This is found to be a simple and very efficient method of generating these systems, and can be used for more complicated cases as shown in Scheme 64.



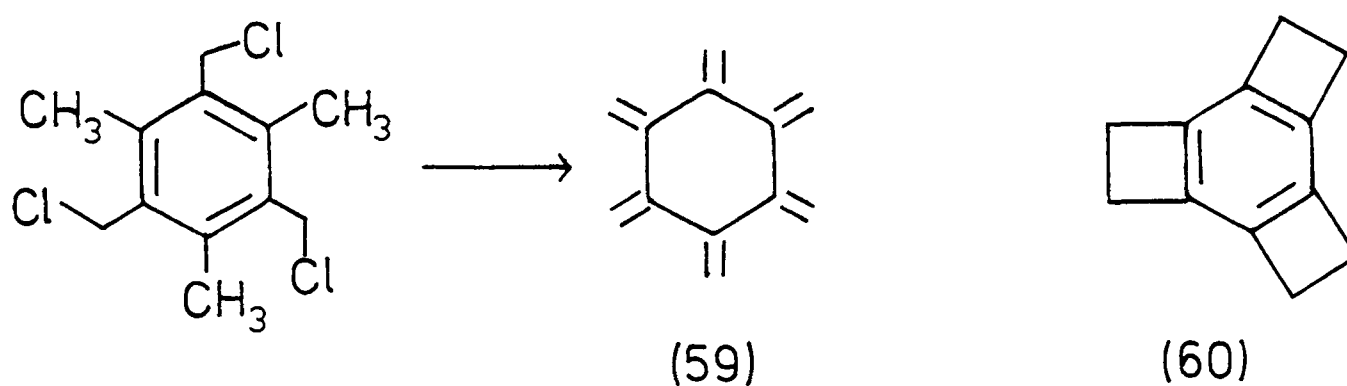
Scheme 64

A variety of benzodicyclobutenes have also been prepared albeit in somewhat lower yields.^{86,88}

This approach can also be applied to heteroaromatic systems for example [2,3:5,6]dicyclobutapyridine has been prepared⁸⁹ (Scheme 65).

Scheme 65

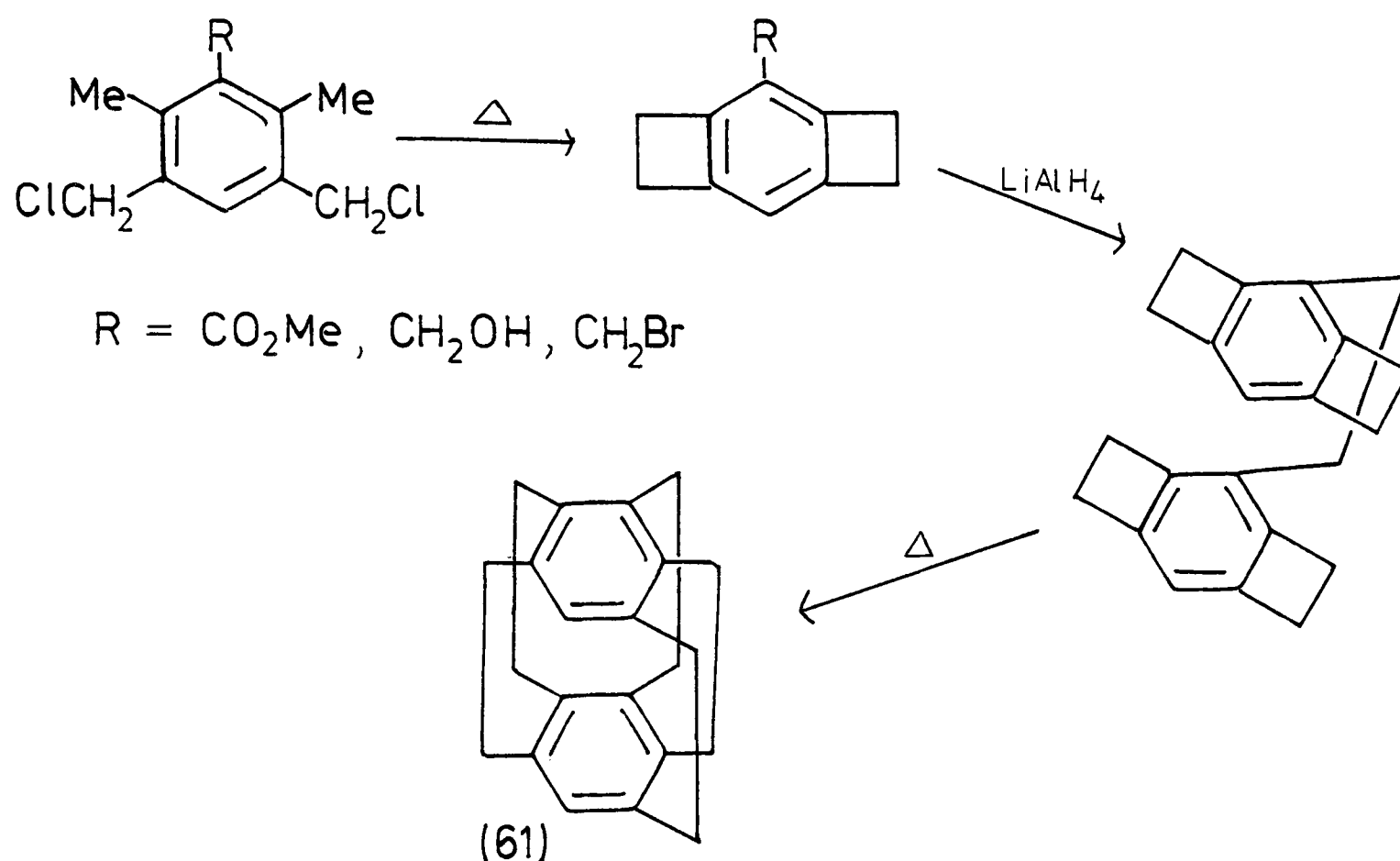
However, attempts to prepare benzotricyclobutene in a similar fashion, result in the formation of hexaradialene (59), although any involvement by the benzotricyclobutene as

Scheme 66

an intermediate has not been ruled out (Scheme 66).^{90,91}

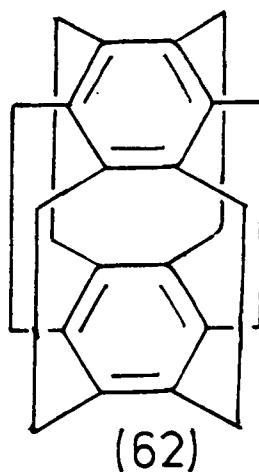
In general, one of the most important properties of the various benzocyclobutenes is their ability to ring open to the appropriate diene which can then undergo further reaction e.g. dimerisation. The concept of using this dimerisation to introduce multiple bridges in cyclophanes was first proposed

by Boekelheide in 1978.⁹² The basic idea has subsequently been demonstrated by the simple, practical synthesis of [2.2.2.2] (1,2,4,5)cyclophane⁹³ and [2.2.2.2.2] (1,2,3,4,5)-cyclophane (61).⁹⁴



Scheme 67

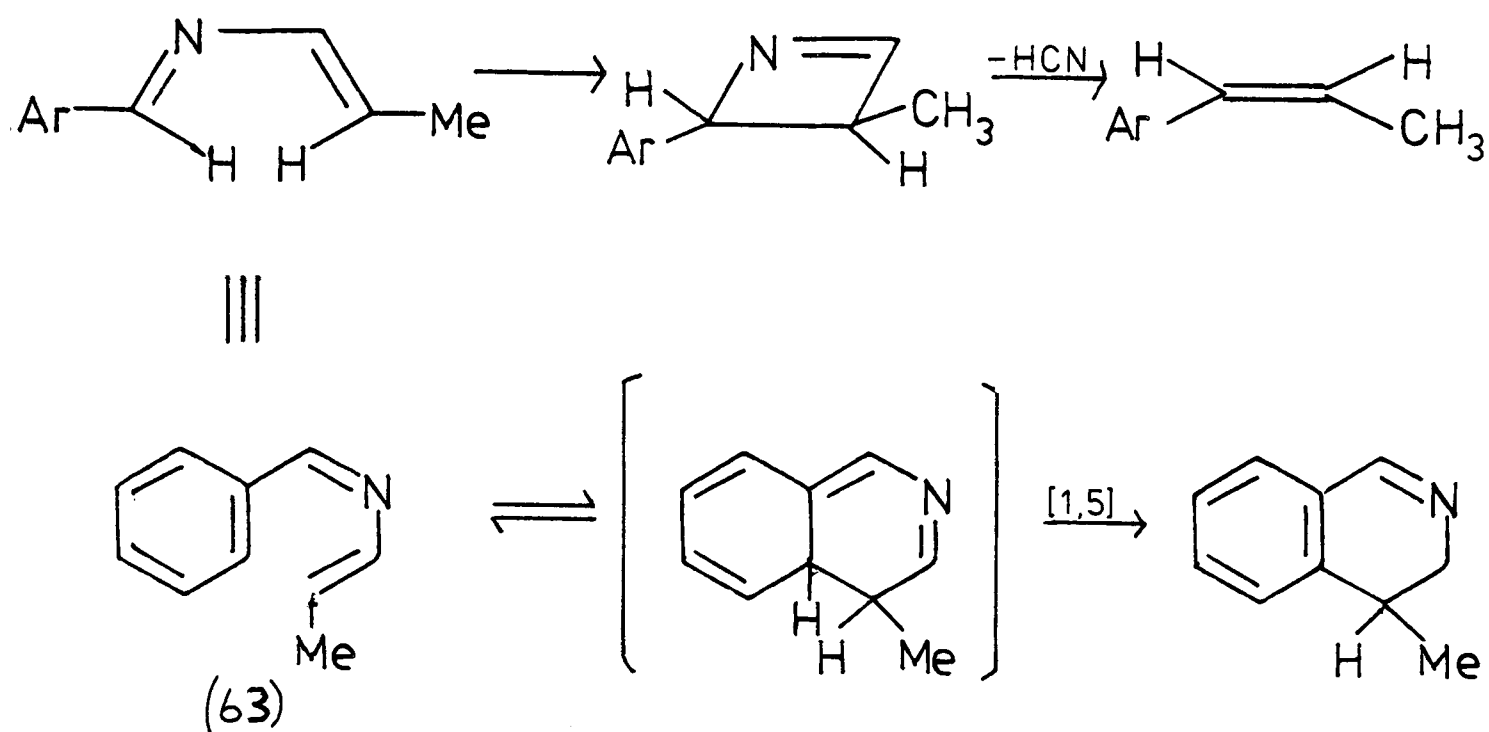
These highly efficient and relatively short syntheses have now been extended to enable the synthesis of superphane (62).⁹⁵



Alternatively, intramolecular trapping of the benzo-cyclobutene has been used in alkaloid synthesis.⁹⁶

2. Azabutadienes

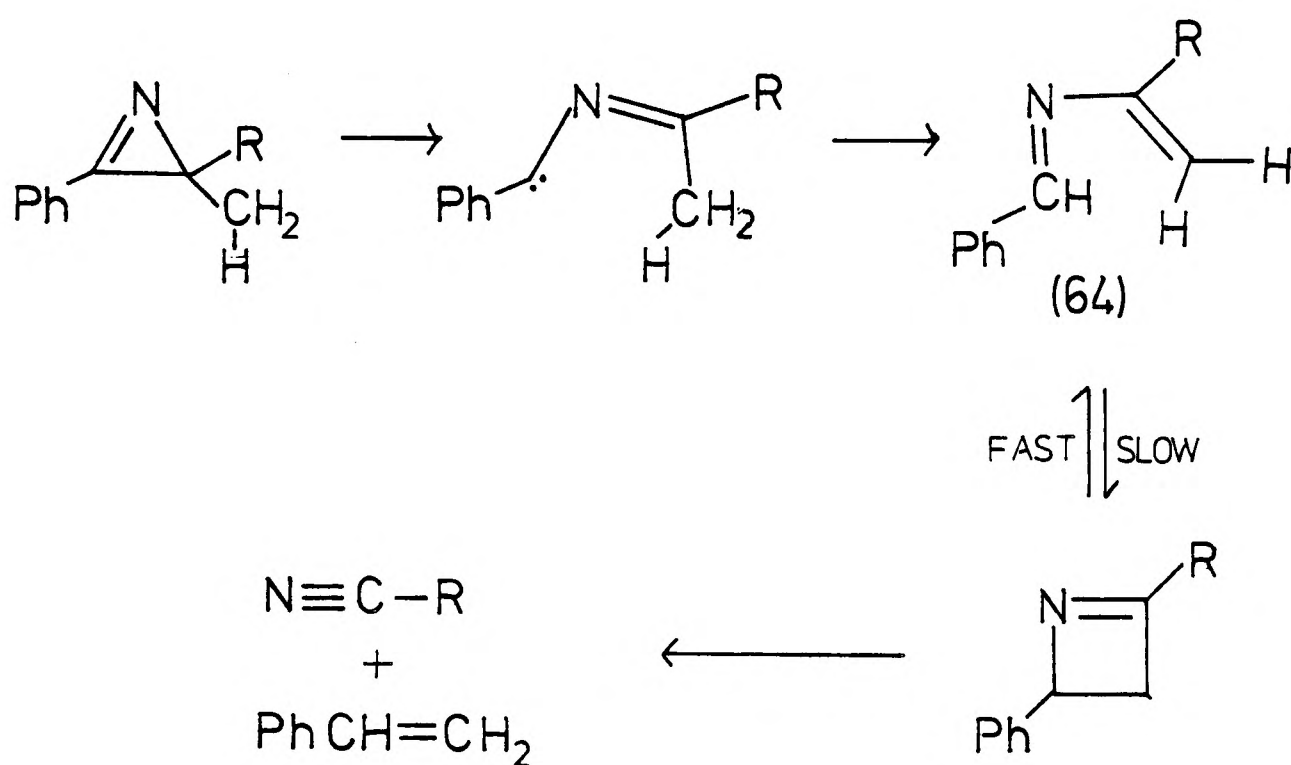
The majority of reactions in which 4π thermal electrocyclicisation of azabutadienes takes place is followed by cleavage of a nitrile from the azetine to give an alkene.



Scheme 68

For example, Taylor and Govindan⁴⁹ found two competing reactions on pyrolysis of the azadiene (63). The 6π thermal electrocyclicisation, as previously discussed, was in competition with a 4π electron electrocyclicisation which gave a 1-azetine intermediate (Scheme 68) which then fragmented with loss of hydrogen cyanide to give 1-propenyl arene. While 1-azetine itself gives 2-aza-1,3-butadiene and does not give HCN on pyrolysis,⁹⁷ in the present case C-N cleavage would give a transition state stabilised by benzylic conjugation.

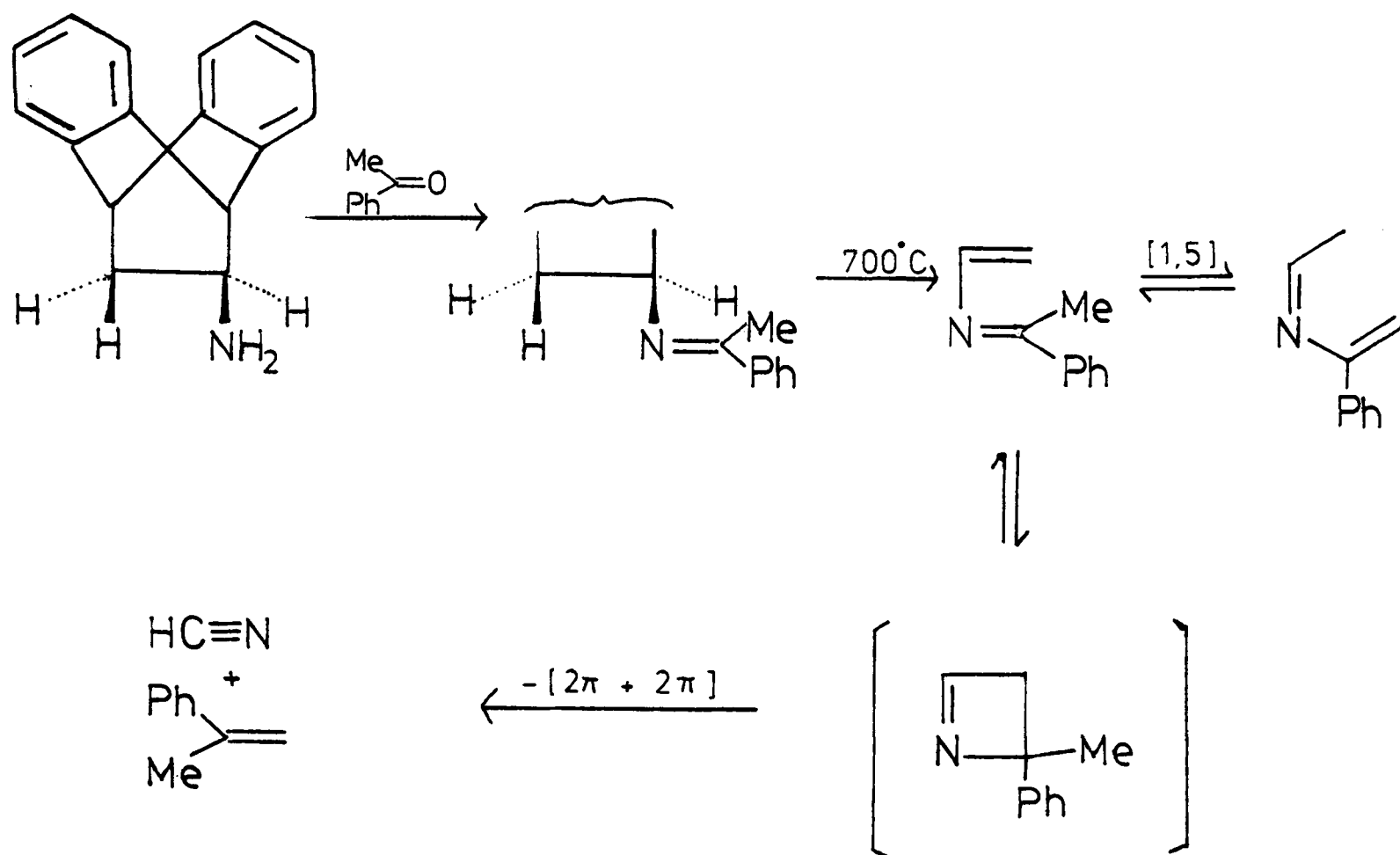
There have been earlier findings of a similar nature reported in the literature. Wendling and Bergman,⁴⁸ for example, have investigated the thermal decomposition of 2H-azirines, (Scheme 69).

Scheme 69

They believe that the azabutadiene (64) is formed by a 1,4-hydrogen abstraction of the vinyl carbene or 1,3-diradical-like species, generated from the thermal ring opening of the substituted cyclopropene. An endothermic thermal electrocyclisation may then generate a small steady state amount of azetine which fragments to the observed products. Further evidence for this type of reaction has been published,⁹⁸ and will be discussed in more detail in the next section of this thesis.

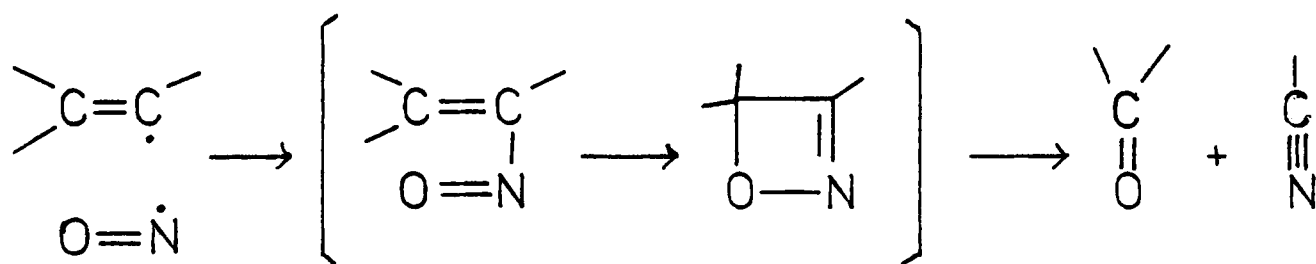
Ripoll and co-workers⁹⁹ have also found that when a dienic system, conjugated with a phenyl group, undergoes flash thermolysis, then a cleavage reaction involving $[2\pi+2\pi]$ processes, takes place in most cases (Scheme 70).





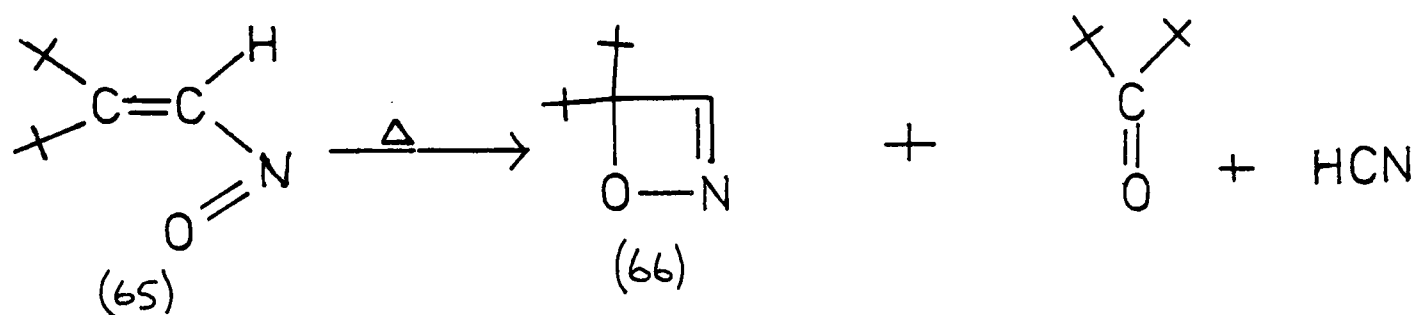
Scheme 70

Hetero 2-azadienes apparently fragment in a similar manner. Derivatives of 4H-oxazetes have been postulated as reactive intermediates in the formation of carbonyl compounds and nitriles, from vinyl and nitrosyl radicals (Scheme 71).^{100,101}



Scheme 71

However, Wieser and Berndt,¹⁰² have prepared a nitrosoalkene (65), which is stable at room temperature due to the introduction of bulky substituents.

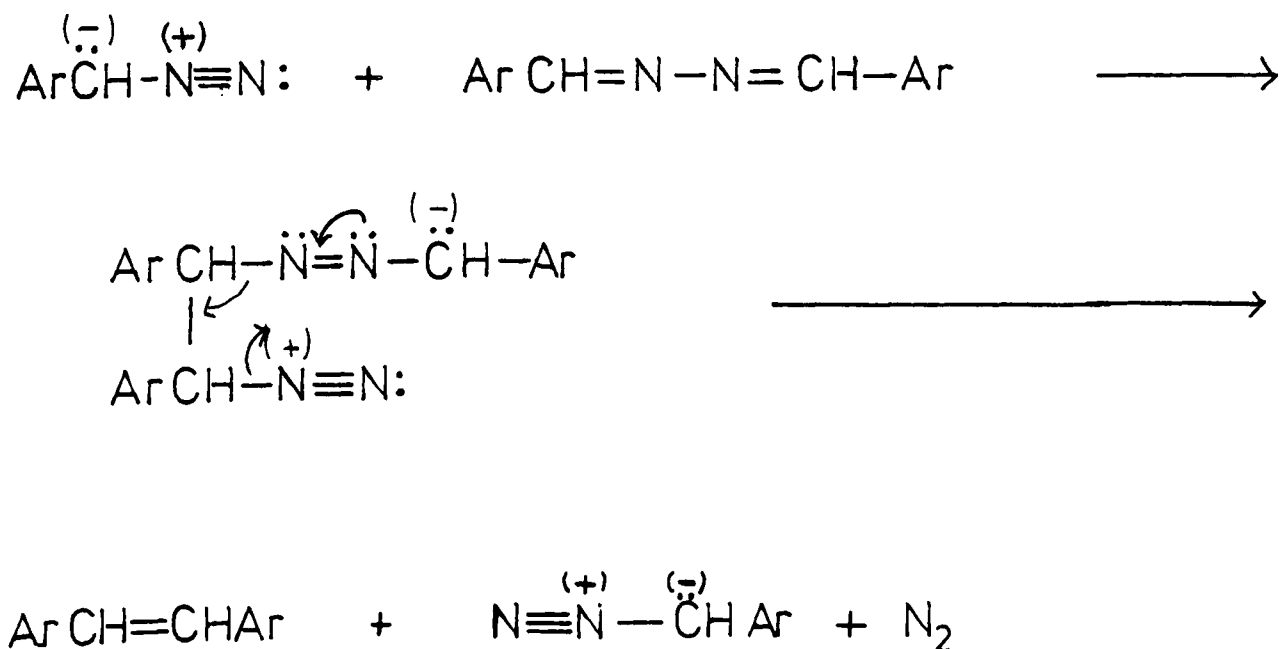
Scheme 72

Flash thermolysis of (65) at 220°C and 10^{-4} Torr affords the oxazete (66) in 54% crude yield. Further fragmentation of the oxazete gives di-*tert*-butylketone and hydrogen cyanide, the sole products above 240°C.

3. Azines

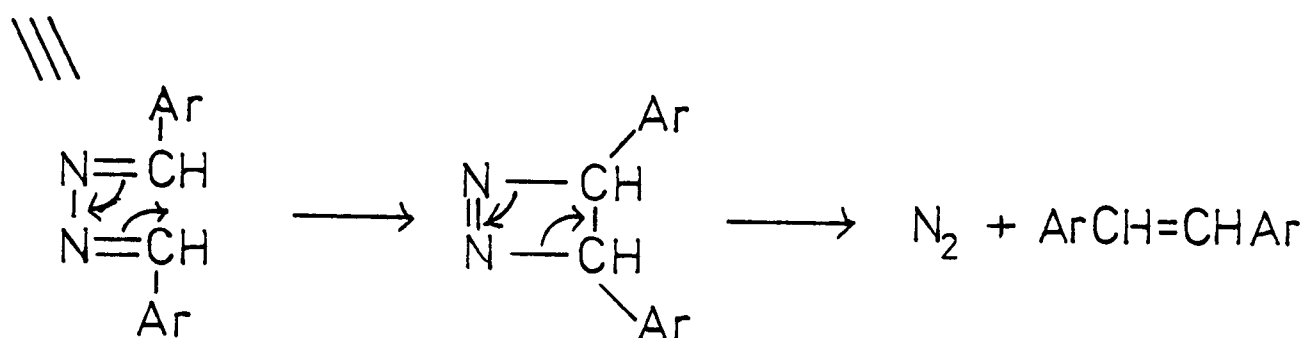
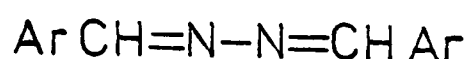
There has been considerable interest in the pyrolysis of azines, which are 2,3-azabutadienes. A range of products are obtained which are hard to rationalise by a single mechanism.

The thermal decomposition of aldazines has been studied by Zimmerman and Somasekhara¹⁰³ in the condensed phase and shown to give stilbenes, and they propose that the reaction takes place *via* an aryldiazomethane intermediate (Scheme 73).

Scheme 73

However, the initial formation of phenyldiazomethane in a gas phase unimolecular decomposition, would not be expected on thermochemical grounds. Should it occur, one would expect to be able to identify the known reaction products¹⁰⁴ from the phenyl carbene which must constitute the other fragment.

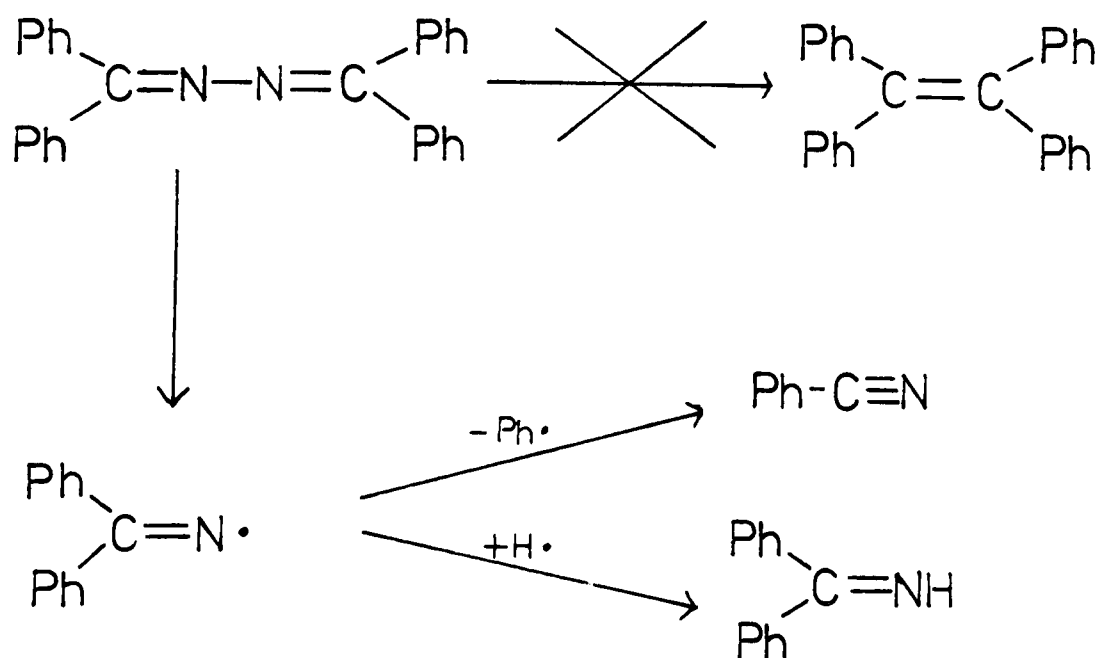
A more likely explanation for the reaction that Zimmerman and Somasekhara found taking place would be as shown in Scheme 74.



Scheme 74

As has been shown previously, there is considerable precedence for this type of reaction taking place.^{48,49,99,102}

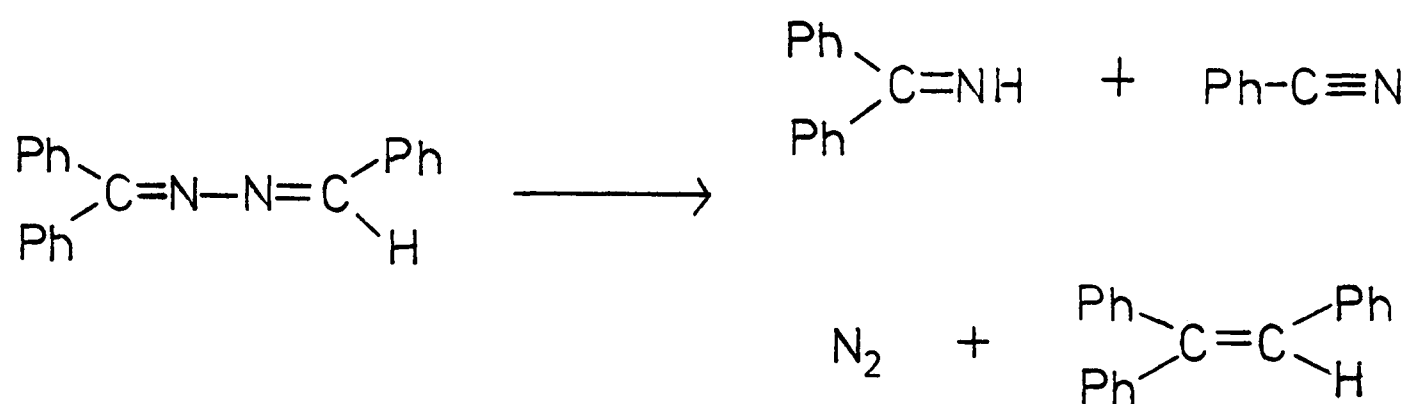
Hirsch¹⁰⁵ expected flash pyrolysis of benzophenone azine to give tetraphenylethylene as the major product, in analogy to the formation of stilbene from benzal azine.



Scheme 75

However, he found (using a direct pyrolyser \rightarrow g.c. system) that benzophenone azine decomposed by a free radical mechanism to give the products shown in Scheme 75.

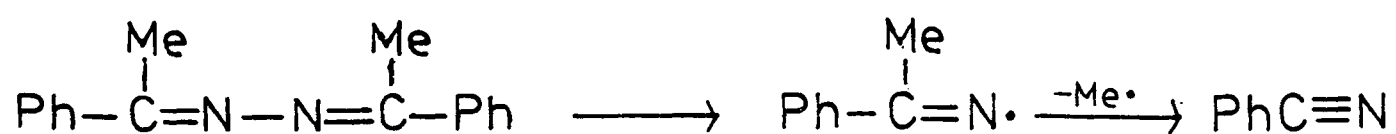
In view of the entirely different principal courses of pyrolysis of the structurally related aldazines and the ketazine, it was of interest to determine the decomposition of the half aldazine half ketazine, benzhydrylidene-benzylidene azine upon thermolysis.



Scheme 76

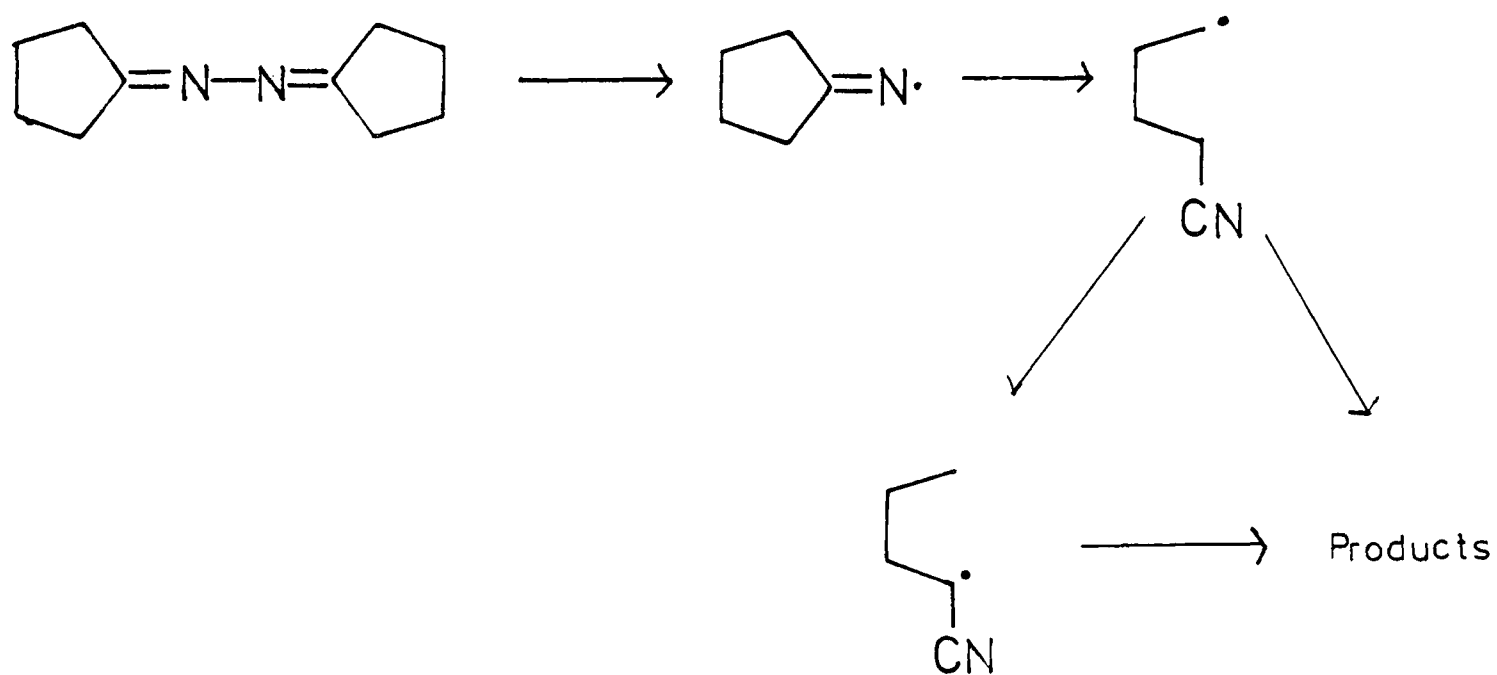
It was found that benzophenone imine and benzonitrile were present (as obtained from benzophenone azine) but so also were N_2 and triphenylethylene (Scheme 76). This suggests that both free radical and molecular mechanisms participate in the reaction.

Crow and co-workers^{106,107} have also carried out gas phase pyrolyses of several azines. They postulate that the weak central N-N bond of the azine molecule cleaves to give iminyl radicals which leads to the formation of nitriles in varying yields, (e.g. Scheme 77).

Scheme 77

Both aryl aldehyde and aryl ketone azines give aryl cyanides in contrast to earlier work by Zimmerman and Somasekhara.¹⁰³ In general, high yields were obtained using ketone azines (e.g. Scheme 77) as would be expected because it is known that alkyl radicals are better leaving groups than hydrogen atoms.

Crow has also carried out work on the pyrolysis of cyclopentanone and cyclohexanone azine¹⁰⁷ to give cyclic iminyl radicals which undergo fragmentation of the ring system to give cyanoalkyl radicals. After various fragmentation and coupling reactions, many different nitrile products are obtained (e.g. Scheme 78).

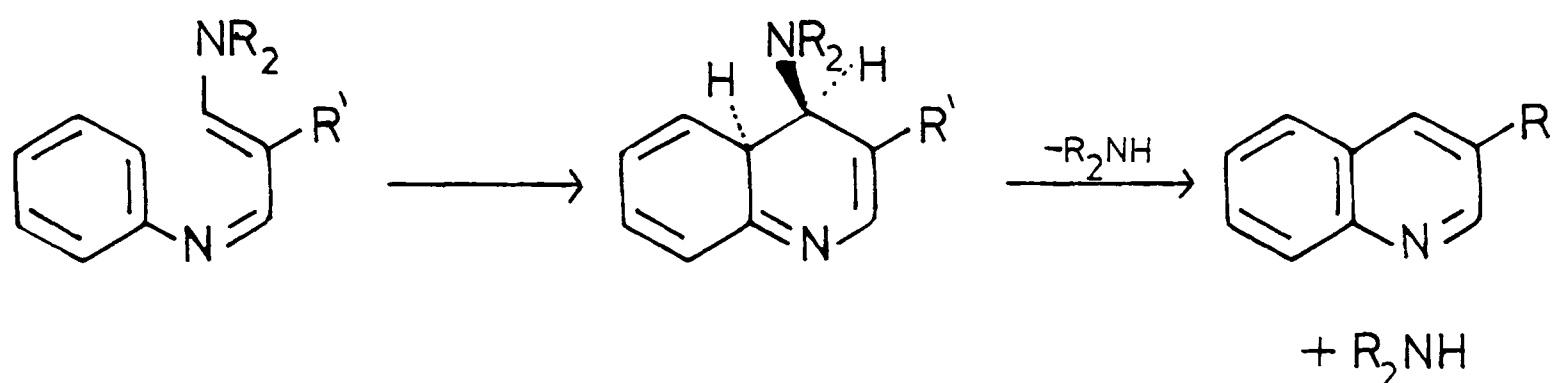
Scheme 78

DISCUSSION

A. PREPARATION AND PYROLYSIS OF 1,5-DIAZAPENTADIENES

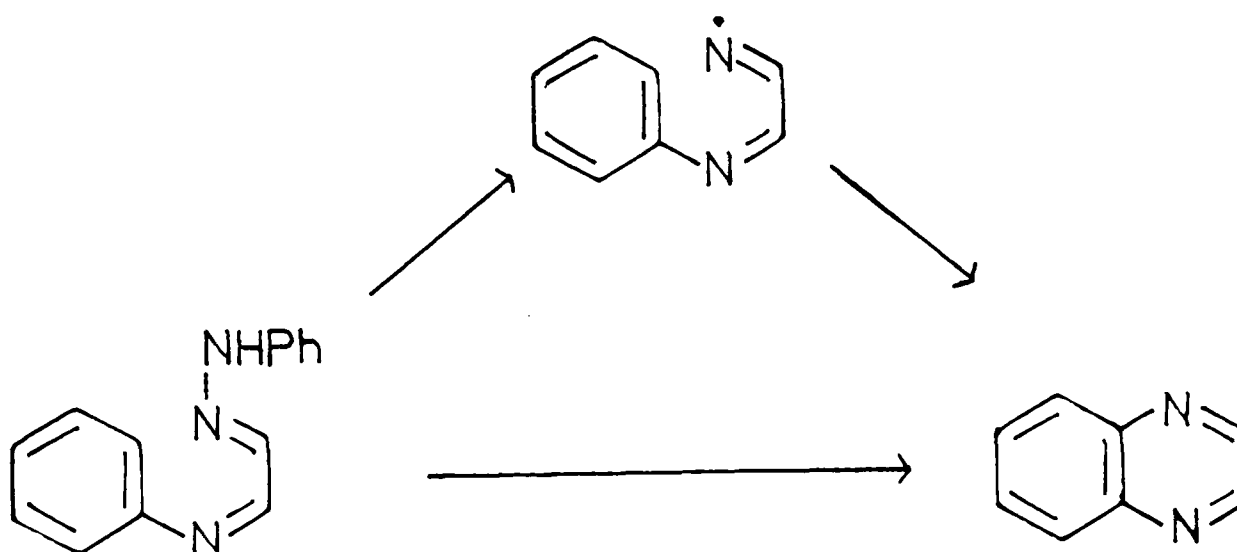
I. PREPARATION OF 1,5-DIAZAPENTADIENES

As discussed previously, solution pyrolysis of 1,5-diazapentadienes provides an efficient synthesis of quinolines by electrocyclic ring closure followed by elimination.⁵²



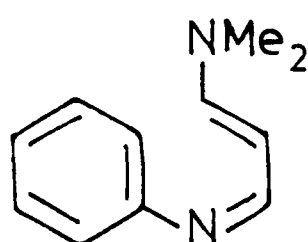
Scheme 79

Previous work has also shown that flash vacuum pyrolysis of 1,5-diaryl-1,2,5-triazapentadienes yield quinoxalines (albeit by a conjugated iminyl radical).^{64,66}

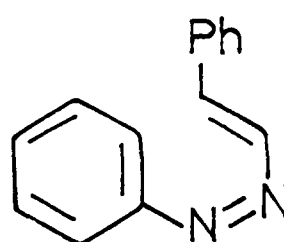


Scheme 80

It was therefore of particular interest to discover that gas phase thermolyses of related systems (eg. (67) and (68)) did not result in the 1-aryl ring being involved in the major reaction pathway: an understanding of these reactions was a major objective of the work described in this thesis.



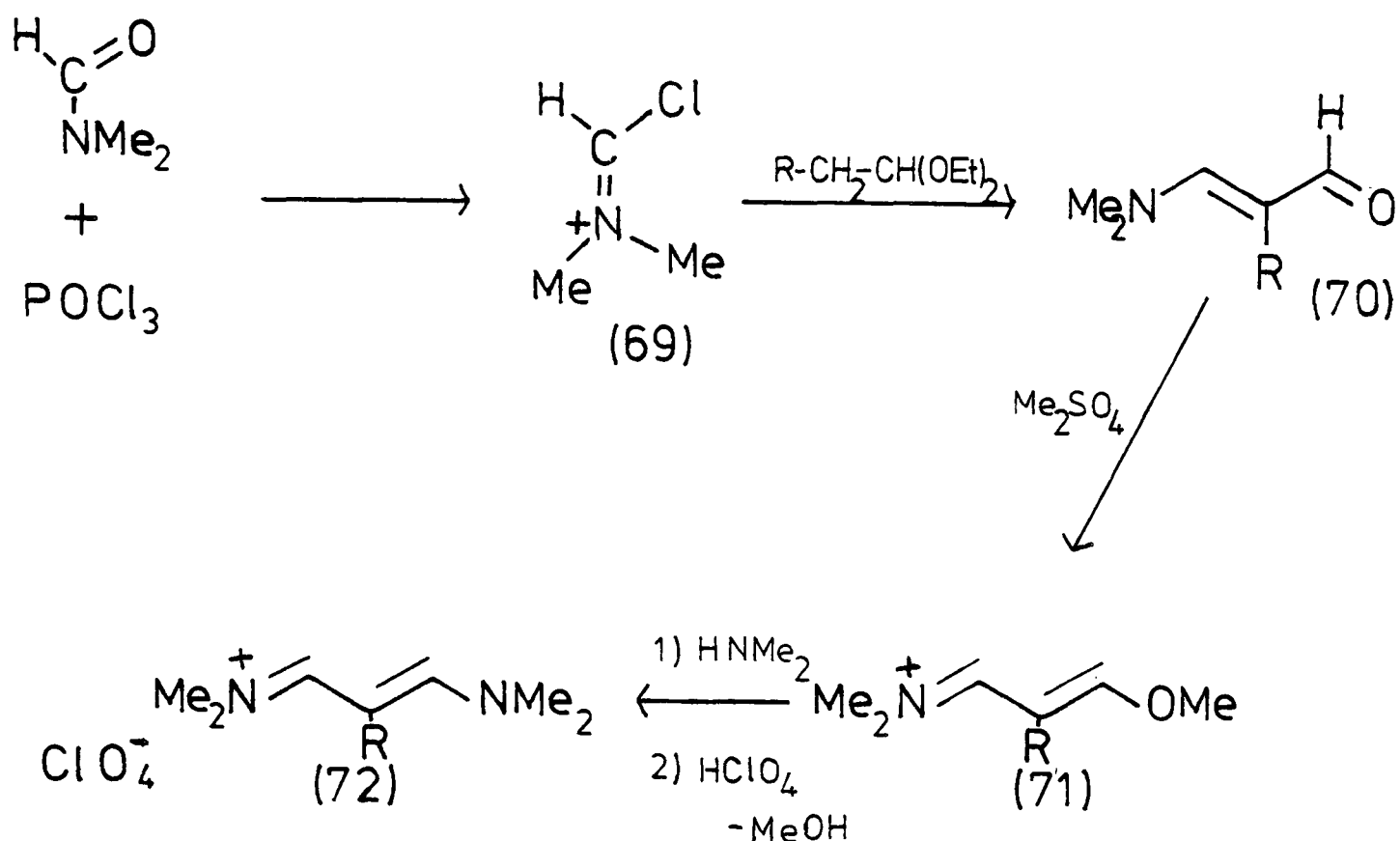
(67)



(68)

Compounds such as (67) are known either as 1,5-diazapentadienes or vinamidines and are effectively derivatives of malondialdehydes and related compounds e.g. mono or bisacetals of 1,3-dicarbonyl compounds. There are two general routes into diazapentadienes.^{52,53}

Jutz found an effective method of formation of vinamidinium salts consisted of using the Vilsmeier-Haack-Arnold formylation reagent¹⁰⁸ (69) (formed by the action of phosgene or phosphoryl chloride on dimethylformamide). This was then used to treat acetaldehyde acetals and homologues¹⁰⁹ (or the corresponding enol ethers) to give 3-dimethylaminoacroleins (70) in high yields. Alkylation of (70) gives the intermediate 3-alkoxyallylidene ammonium salts (71) which are converted to the vinamidinium salts (72) with dimethylamine.^{56,110,111} This method is readily adapted to large scale preparations.

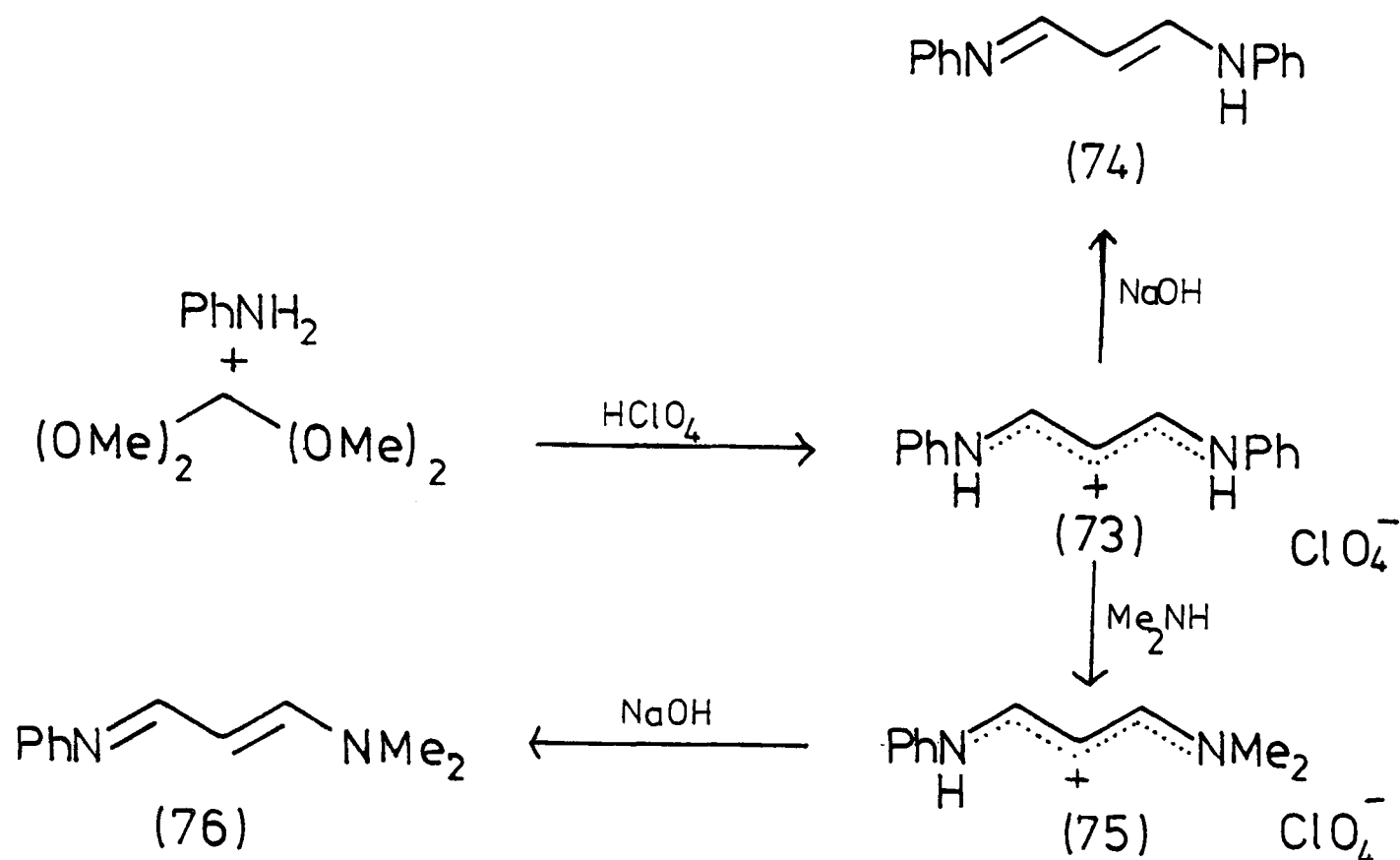


Scheme 81

A more convenient route to vinamidinium salts is that used by Lloyd, McNab and Marshall⁵³ where the salts are prepared by the reaction of amines with dicarbonyl compounds (or their mono or bisacetals) and is the method used here. Substituents may be readily incorporated on the carbon chain or heteroatoms readily substituted for carbon. The amine substituents are also easily varied as the amino group can be readily displaced by an amine with a more electron rich nitrogen. For instance, anil groups can be displaced sequentially by dimethylamino groups.

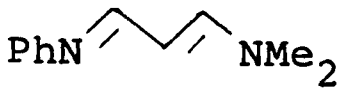
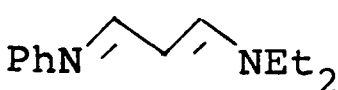
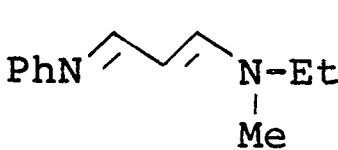
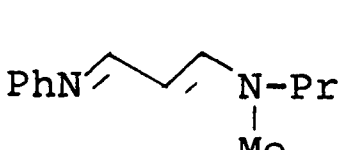
Thus, to prepare 1,1-dimethyl-5-phenyl-1,5-diazapentadiene (76), 1,5-diphenyl-1H-1,5-diazapentadienium perchlorate (73) was made first, by the addition of perchloric acid to a solution of 1,1,3,3-tetramethoxypropane and aniline in ethanol. Treatment with dimethylamine resulted in the rapid formation of 1,1-dimethyl-5-phenyl-1H-1,5-diazapentadienium perchlorate (75)

which was turned into the corresponding diazapentadiene on treatment with sodium hydroxide.

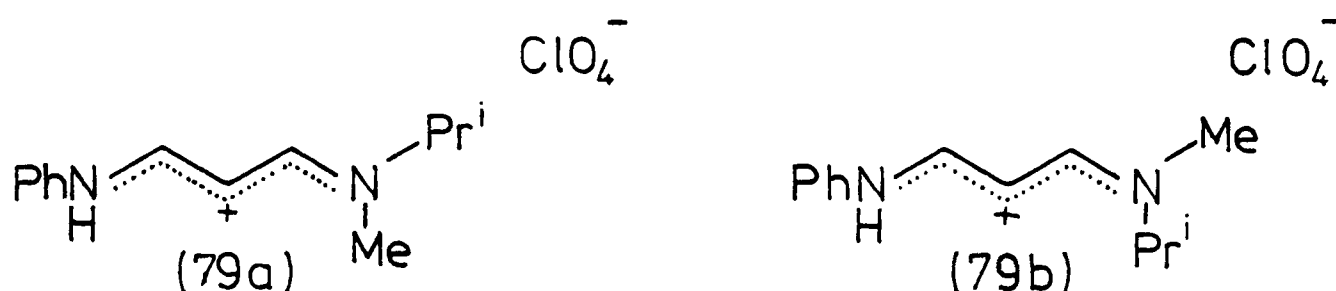


Scheme 82

Three other 1,1-dialkyl-5-phenyl-1,5-diazapentadienes (77), (78) and (79) were made in a similar way using diethylamine, methylethylamine and methyisopropylamine. However the conditions were not always straightforward. For example, to prepare the 1,1-diethyl-5-phenyl-1 H -1,5-diazapentadienium perchlorate, the mixture had to be left to stand overnight before the material precipitated out of solution and attempts to prepare the 1,1-diisopropyl analogue were unsuccessful. Perhaps the difficulties encountered in preparing the diethyl and the diisopropyl compounds are due to the steric bulk of the ethyl and isopropyl group.

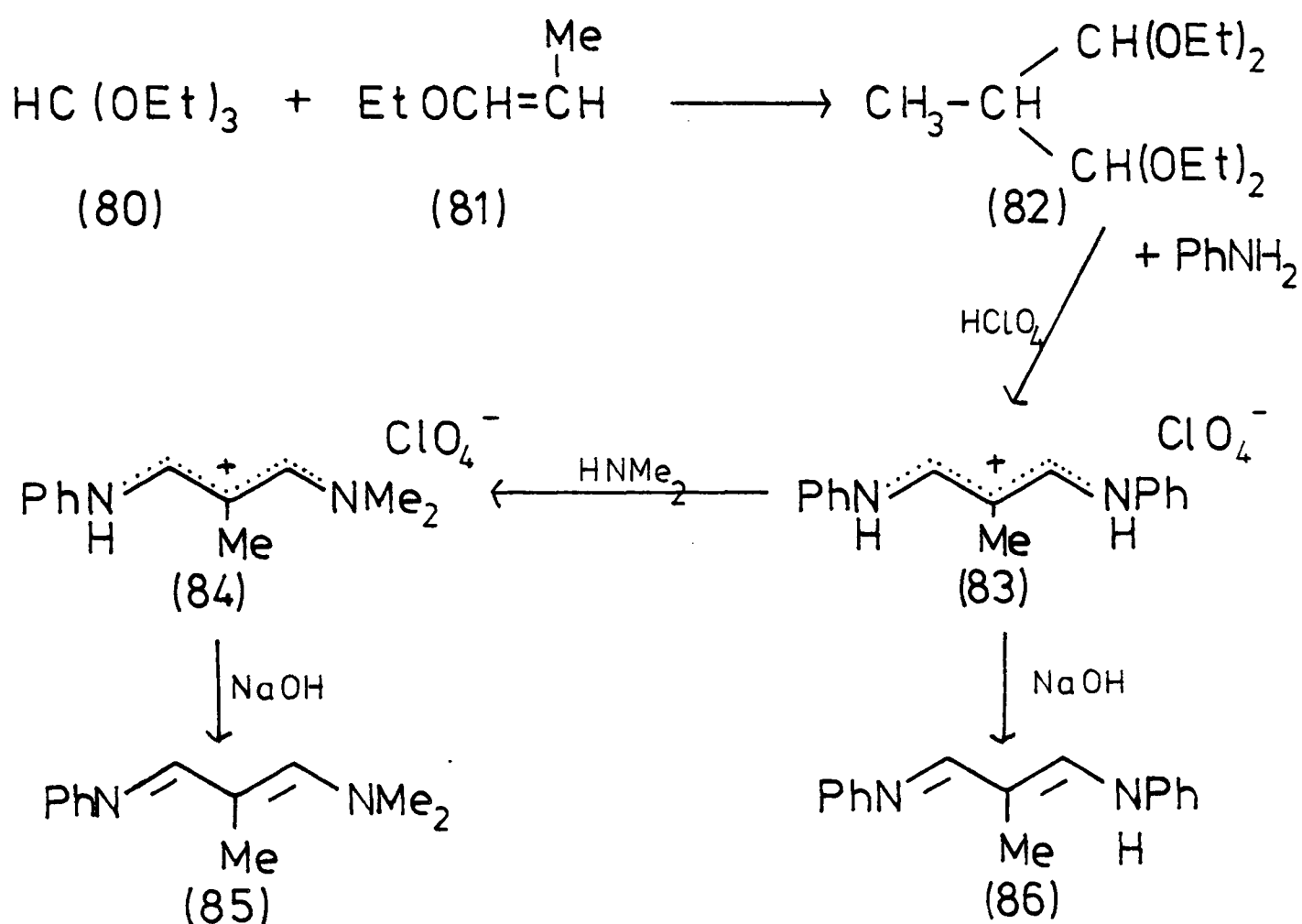
	<u>Perchlorate</u> <u>Yield</u>	<u>Diazapentadiene</u> <u>Yield</u>	<u>b.p.</u> (0.1 Torr)
 (76)	62%	84%	152-155°C
 (77)	73%	94%	156-159°C
 (78)	79%	92%	130-133°C
 (79)	75%	50%	171-173°C

The ^1H n.m.r. spectra of the perchlorates (78) and (79) showed that there were two isomers present, presumably due to the two possible positions of the alkyl groups.



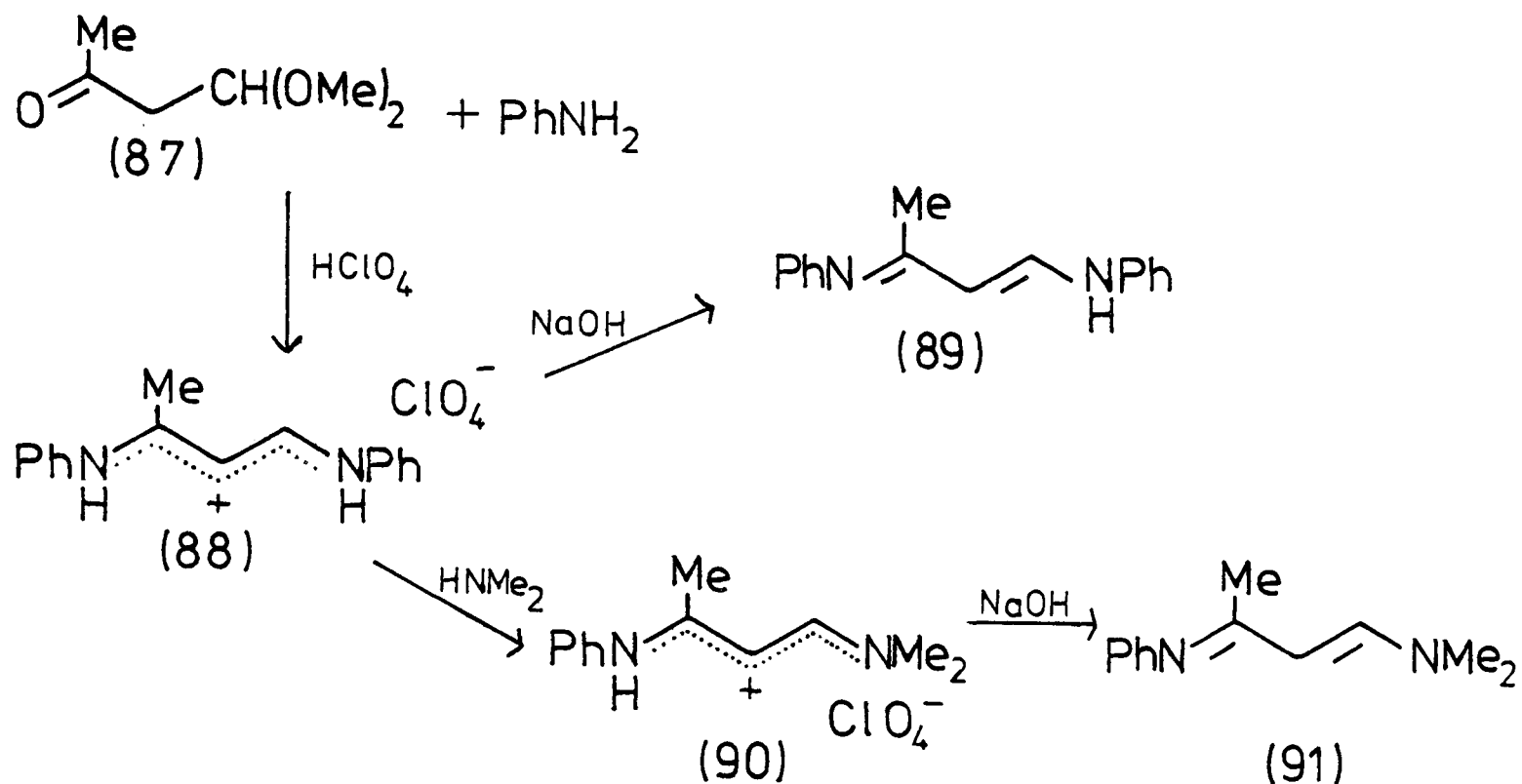
These positions are fixed due to the partial double bond of the nitrogen with the adjacent carbon. However, where there is relatively free rotation around this bond, as in the case with the diazapentadiene, only one isomer is observed. The major isomer present in each case was presumably that with the largest alkyl group in the position furthest from the hydrogen on the central carbon (eg. (a)). A similar strategy was employed to synthesise *C*-methyl diazapentadienes. Methyl-malondialdehyde tetraethyldiacetal (82) was made by reaction

of triethylorthoformate (80) with ethyl propenyl ether (81) using boron trifluoride as a catalyst. Once formed, this then underwent a series of reactions similar to that of 1,1,3,3-tetramethoxy propane above, to give the desired product 5-phenyl-1,1,3-trimethyl-1*H*-1,5-diazapentadiene (85) (Scheme 83).



Scheme 83

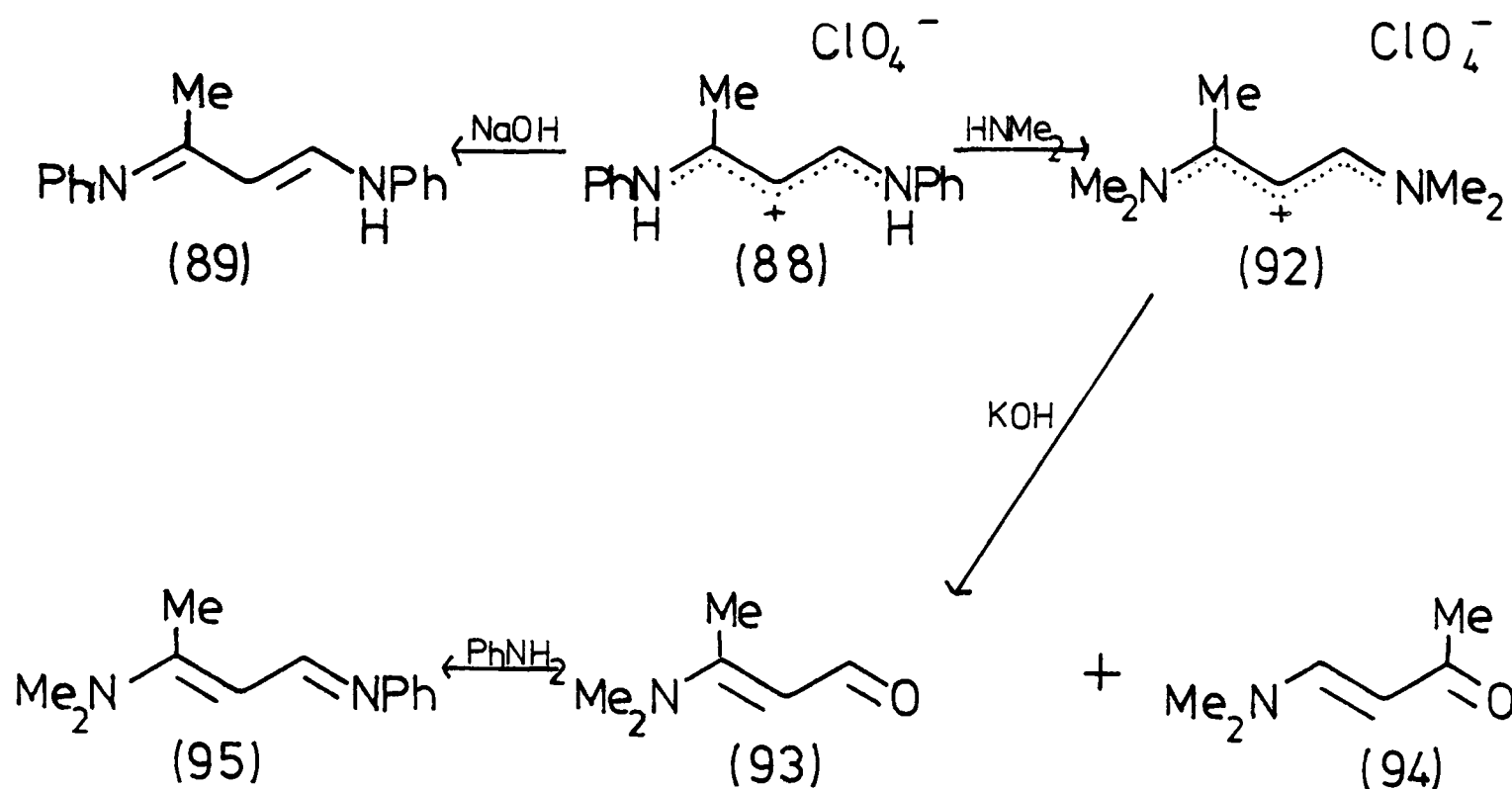
By treating a solution of 3-ketobutyraldehyde-1-dimethyl-acetal (87) and aniline in ethanol with perchloric acid (Scheme 84), 1,5-diphenyl-2-methyl-1*H*-1,5-diazapentadienium perchlorate (88) was formed. Treatment of (88) with dimethylamine resulted in the formation of the perchlorate salt (90) which, when treated with sodium hydroxide yielded 1,1,4-trimethyl-5-phenyl-1,5-diazapentadiene (91).



Scheme 84

It is interesting that the dimethylamine reacts exclusively at one end of the molecule. This is due to the steric and electronic effects of the methyl group which effectively hinders the approach of the dimethylamine.

Replacement of the second anilino group is possible under stronger conditions (eg. overnight stirring). These conditions were required for the preparation of 5-phenyl-1,1,2-trimethyl-1,5-diazapentadiene (Scheme 85). When the perchlorate salt (92) was treated with potassium hydroxide, the acrolein (93) was formed as the major product, along with the ketone (94) as a minor product, due to the expected selectivity of the reaction. When this mixture of aldehyde and ketone was treated with aniline, only the more reactive aldehyde reacted to give the desired product. In this way, the same starting material (88) can be used to prepare the two different trimethyl diazapentadienes (91) and (95) by control of the selectivity of the reactions.

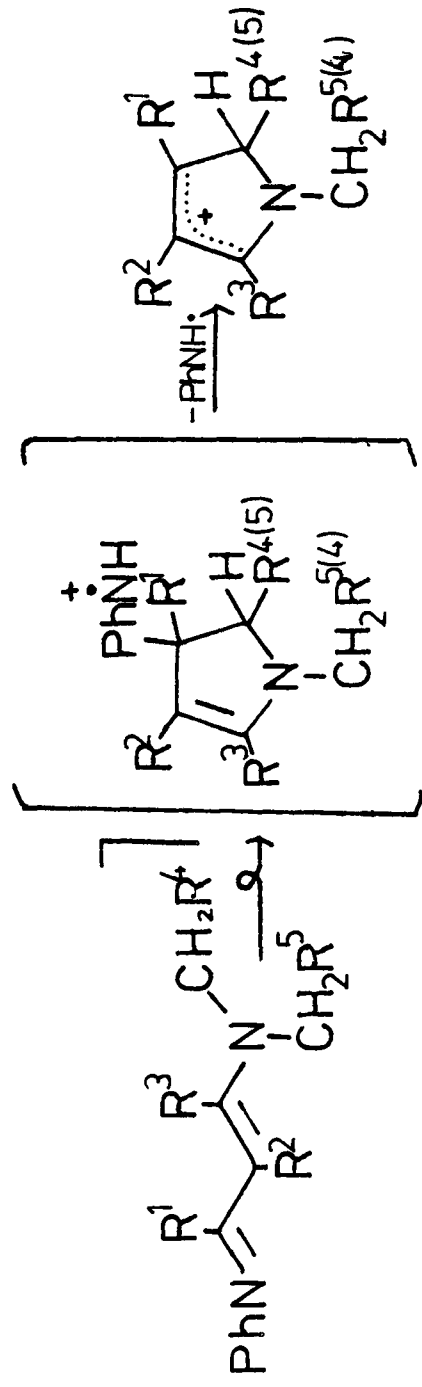


Scheme 85

1,5-Diphenyl-2-methyl-1,5-diazapentadiene (89) and 1,5-diphenyl-3-methyl-1,5-diazapentadiene (86) were also formed by treatment of the appropriate perchlorates, (88) and (83) respectively, with base. The ¹³C n.m.r. spectrum for the 3-methyl compound (86) was interesting in that only five signals appeared to be visible. There was no signal for the methyl group, or for its quaternary carbon, although this could possibly overlap with the signals due to the phenyl. This was shown to be independent of field strength and temperature. There was also a broad signal for carbons (2) and (4) and this was thought to be due to a rapid exchange process involving the proton attached to the nitrogen. The peculiar apparent lack of signal due to the methyl carbon may be caused by a particularly long relaxation time as, with a long pulse delay, a very broad peak is observable.

The mass spectra of the 1,1-dialkyl-5-phenyl-1,5-diazapentadienes are dominated by the loss of an anilino radical to give the pyrrolium cation as shown in Table 1. This route most probably involves hydrogen transfer from an *N*-alkyl

The Mass Spectra Breakdown of 1,5-Dialkyl-1,5-diazapentadienes

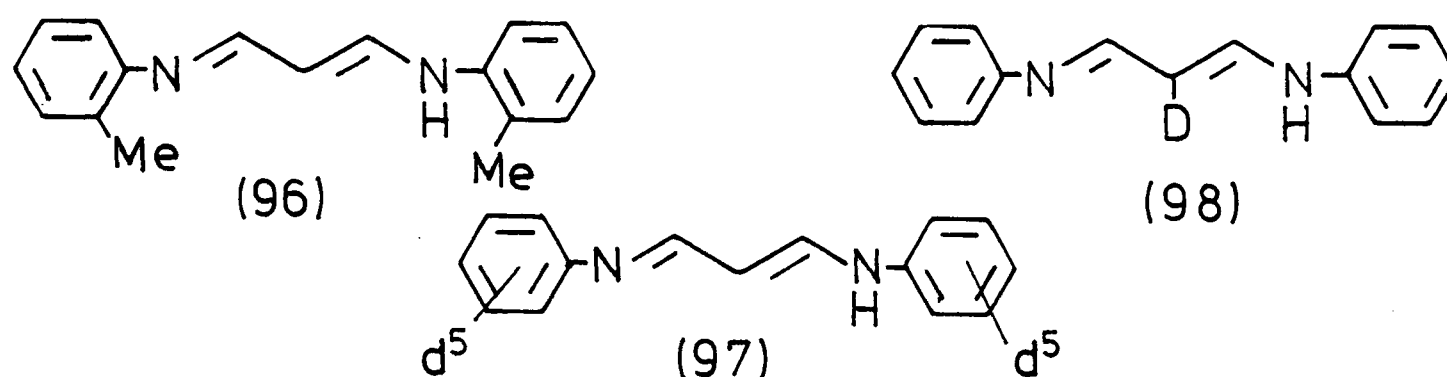


	R ¹	R ²	R ³	R ⁴	R ⁵	m/z	%	m [*]	m/z	%
(76)	H	H	H	H	H	174	15		82	100
(77)	H	H	H	Me	Me	202	53	60	110	100
(78)	H	H	H	H	Me	188	48		96	100
(79)	H	H	H	H	Et	202	39	60	110	100
(85)	H	Me	H	H	H	188	44	49	96	100
(91)	Me	H	H	H	H	188	44	49	96	100
(95)	H	H	Me	H	H	188	12	49	96	35

Table 1

group,¹¹² analogous to the thermal pathway which is to be discussed later.

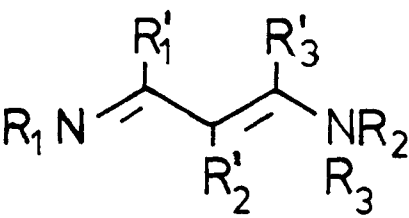
Other diazapentadienes prepared in the same manner as the parent compound (74) (Scheme 82), include 1,5-di-*o*-tolyl-1,5-diazapentadiene (96) (using *o*-toluidine) and 1,5-di[²H₅]phenyl-1,5-diazapentadiene (97) (using [²H₅]aniline).



[3-²H]-1,5-Diphenyl-1,5-diazapentadiene (90) was prepared by dissolving the corresponding [3-¹H] perchlorate in [²H]-trifluoroacetic acid and neutralising with a solution of sodium deuterioxide (deuterioxide was used in place of hydroxide to prevent any back exchange). There was the possibility that the deuterium could have attacked the *para* position on the phenyl rings as conjugated systems like this can undergo electrophilic substitution,¹¹³ due to the activation of the phenyl group by the nitrogen. However, both the ¹H and ²H spectra and the mass spectrum (*m/z* 223) showed that this had not happened.

For easy reference, the 1,5-diazapentadienes which have been prepared are listed in Table 2.

1,5-Diazapentadienes

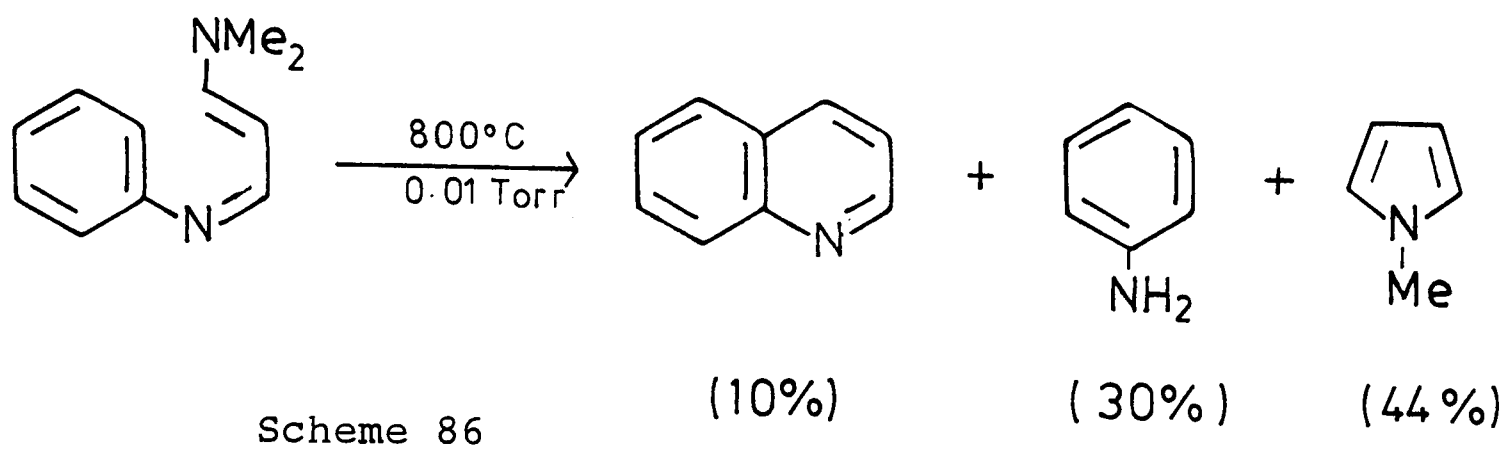


Compound	R ₁	R ₂	R ₃	R' ₁	R' ₂	R' ₃
(74)	Ph	Ph	H	H	H	H
(76)	Ph	Me	Me	H	H	H
(77)	Ph	Et	Et	H	H	H
(78)	Ph	Et	Me	H	H	H
(79)	Ph	Pr ⁱ	Me	H	H	H
(91)	Ph	Me	Me	Me	H	H
(85)	Ph	Me	Me	H	Me	H
(95)	Ph	Me	Me	H	H	Me
(89)	Ph	Ph	H	Me	H	H
(86)	Ph	Ph	H	H	Me	H
(96)	otolyl	otolyl	H	H	H	H
(97)	[² H ₅]Ph	[² H ₅]Ph	H	H	H	H
(98)	Ph	Ph	H	H	D	H

Table 2

II PYROLYSIS OF 1,5-DIAZAPENTADIENES

It was of interest to discover the mechanism for the reaction which took place on pyrolysing 1,1-dimethyl-5-phenyl-1,5-diazapentadiene, as, instead of obtaining quinoline as the major product, as might be expected, it was present only in low yield and the major volatile products were aniline and *N*-methylpyrrole.

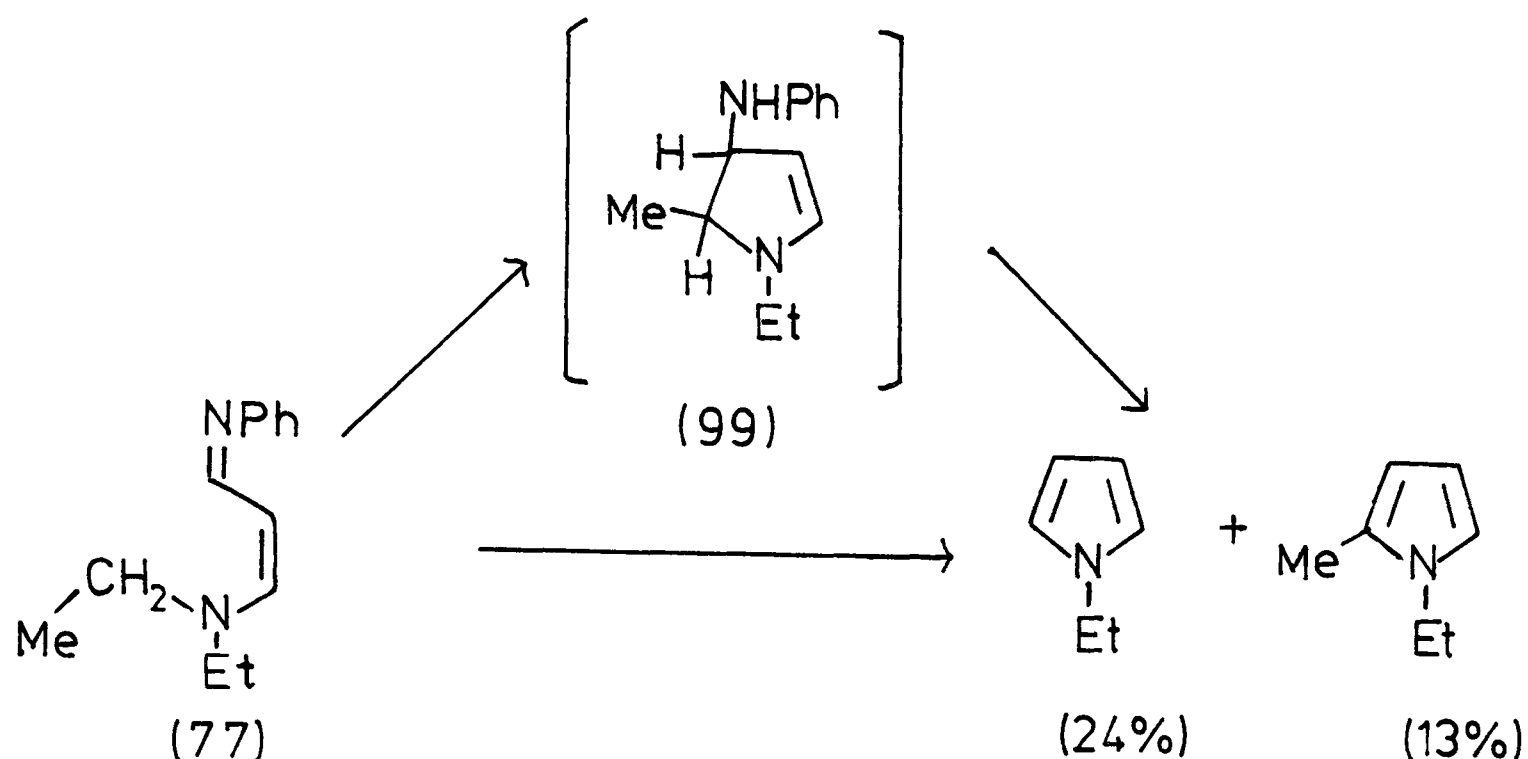


The reaction is particularly surprising as the diazapentadiene is the parent compound of the hexatriene systems used by Jutz⁵² in concerted electrocyclic reactions for the synthesis of quinolines and would therefore be expected to undergo a similar type of reaction.

The flash vacuum pyrolysis of the diazapentadiene was carried out at a furnace temperature of 800°C. The products obtained were *N*-methylpyrrole (44%), aniline (30%) and quinoline (10%). The products were identified using g.c., g.c./m.s. and, by separating out the individual products using preparative gas liquid chromatography, proton n.m.r. spectra of each product were obtained.

It was not clear at this stage what the reaction mechanism was, so the effects of substituents on the nitrogen

and on the carbon chain were studied.



Scheme 87

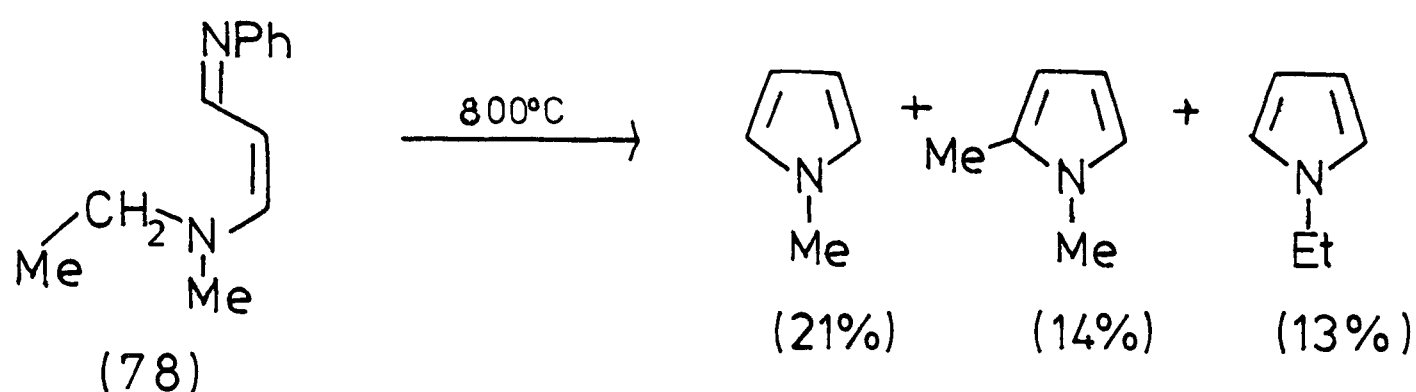
Pyrolysis of the 1,1-diethyl-5-phenyl-1,5-diazapentadiene (77) also gave pyrrole derivatives, but this time two were formed, namely *N*-ethyl-2-methylpyrrole and *N*-ethylpyrrole. The structures of these compounds were established by comparison with samples of authentic pyrroles - the preparation of which is given at the end of this section.

The formation of four functionalised carbons in the pyrrole system would suggest that one of the *N*-alkyl groups must be involved in the cyclisation and this was confirmed by identification of 2-methyl-1-ethylpyrrole in the pyrolysate. However, the formation of 1-ethylpyrrole in even greater yield suggested that the methyl group was being lost by a radical mechanism at the aromatisation step. It is known that in thermal aromatisation reactions alkyl groups cleave by a free radical mechanism more readily than hydrogen atoms.²⁰ This suggests that the reaction was passing through an intermediate (99) as shown in Scheme 87.

It is not possible to tell whether the anilino radical, or the methyl or hydrogen radical is lost first but aniline (41%) and *N*-methylaniline (13%) are obtained by coupling processes.

Pyrolysis of the diethyl compound (77) shows how aromatisation takes place, but because of the cleavage of radicals involved, the reaction will be of little synthetic use as a mixture will always be obtained. However, it was of interest to discover just how the cyclisation step takes place since functionalisation of an unactivated *N*-alkyl group is a very unusual process.

It was the pyrolysis of the diazapentadiene (78) with both an ethyl and a methyl group present on the nitrogen which indicated the most plausible reaction route.

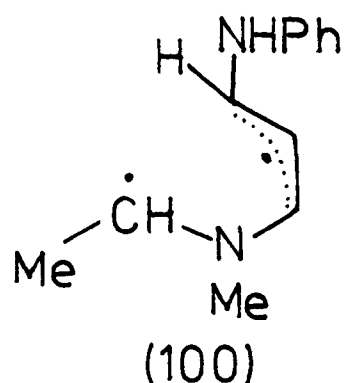


Scheme 88

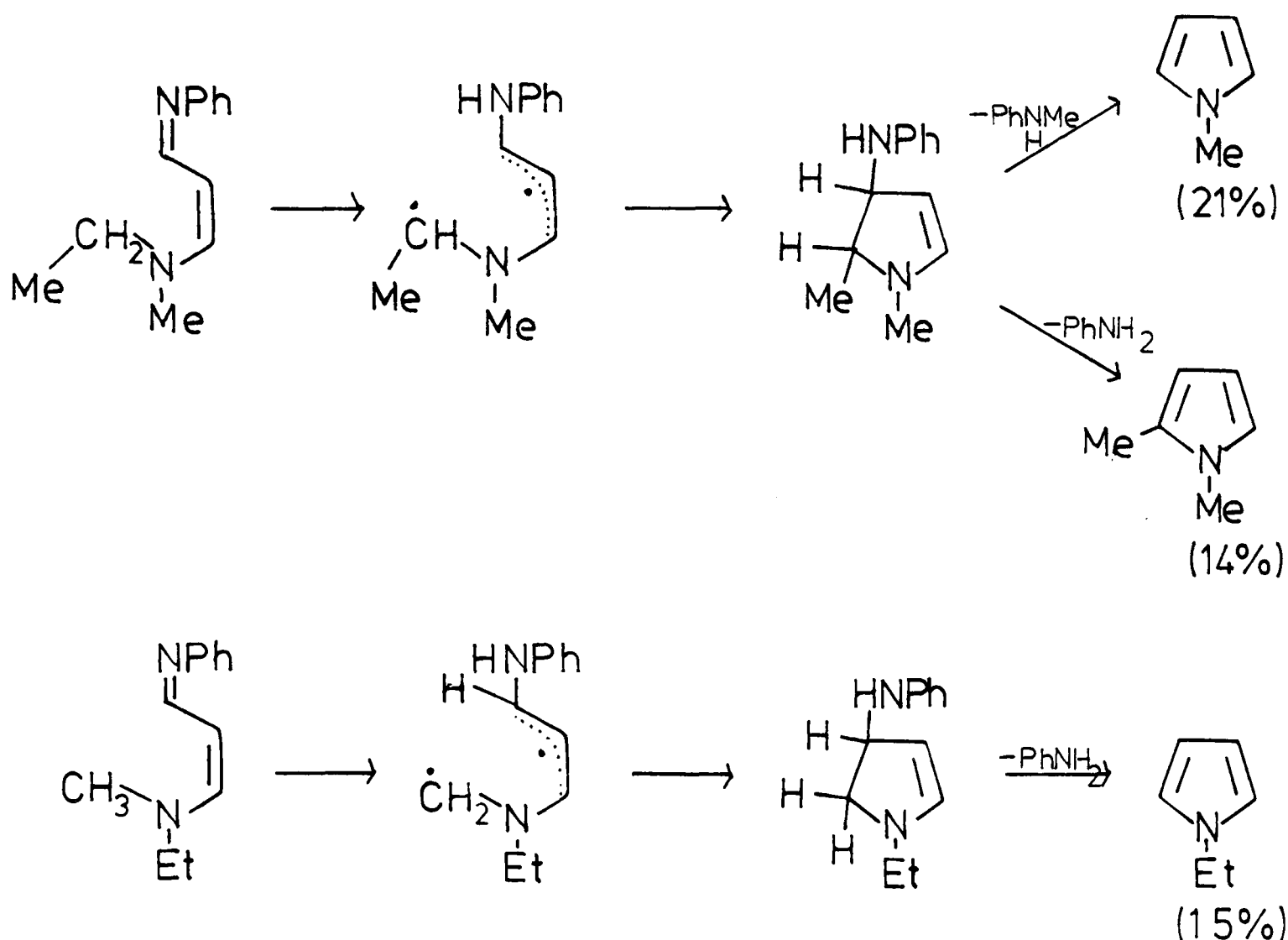
Three pyrroles were formed (Scheme 88). The two *N*-methylpyrroles amounting to about 75% of the pyrrole fraction are formed as above by reaction of the *N*-ethyl group while the *N*-ethylpyrrole is generated by reaction of the *N*-methyl group of the starting material. The secondary site being more reactive than the primary site points to radical intermediates which might be formed by intramolecular hydrogen transfer. This could generate the diradical (100) which is doubly

stabilised by its allyl and α -aminoalkyl fragments.¹¹⁴⁻¹¹⁷

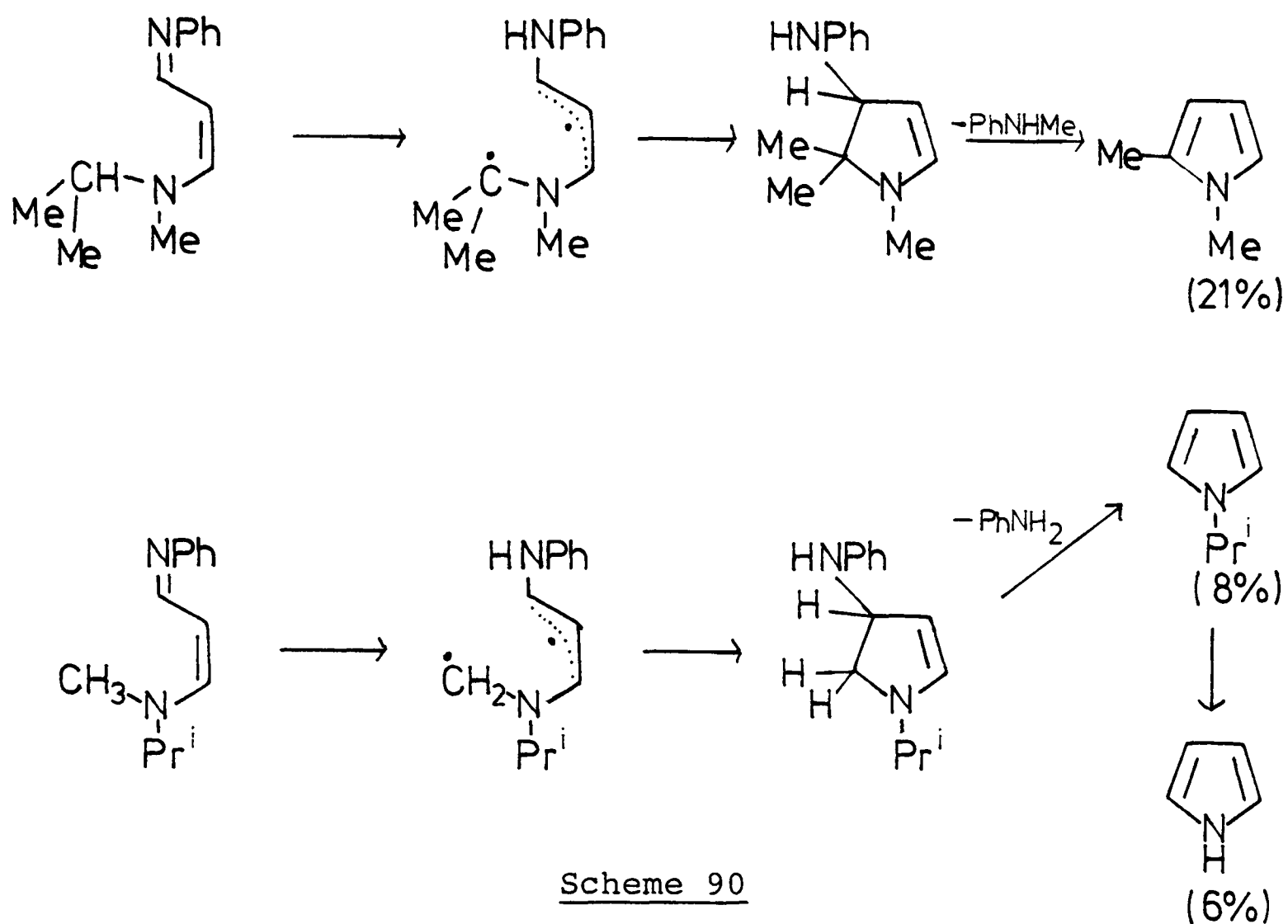
This is an unusual step but the diradical which may be formed would be particularly stable as the unpaired electrons adjacent to the π bond and the electron lone pair on the nitrogen are stabilised by conjugative delocalisation.



There are therefore two competitive reaction pathways, one involving a primary radical intermediate, the other a secondary radical intermediate.



As can be seen from Scheme 89, the majority of the pyrroles (~75%) are formed *via* the secondary radical intermediate due to its greater stability.



Similarly with 1-isopropyl-1-methyl-5-phenyl-1,5-diazapentadiene (79) where the choice is between a primary or a tertiary radical intermediate, the tertiary radical intermediate is preferred (Scheme 90).

In this case the 1,2-dimethylpyrrole and 1-isopropyl pyrrole are formed as expected but in addition pyrrole itself was obtained. This was shown, by independent pyrolysis, to arise by dealkylation of the *N*-isopropyl compound and hence derives from hydrogen transfer at the primary site.

The relative selectivities (primary versus secondary and primary versus tertiary) for the reactions are shown in Table 3

together with the statistical corrections for the number of available hydrogens.

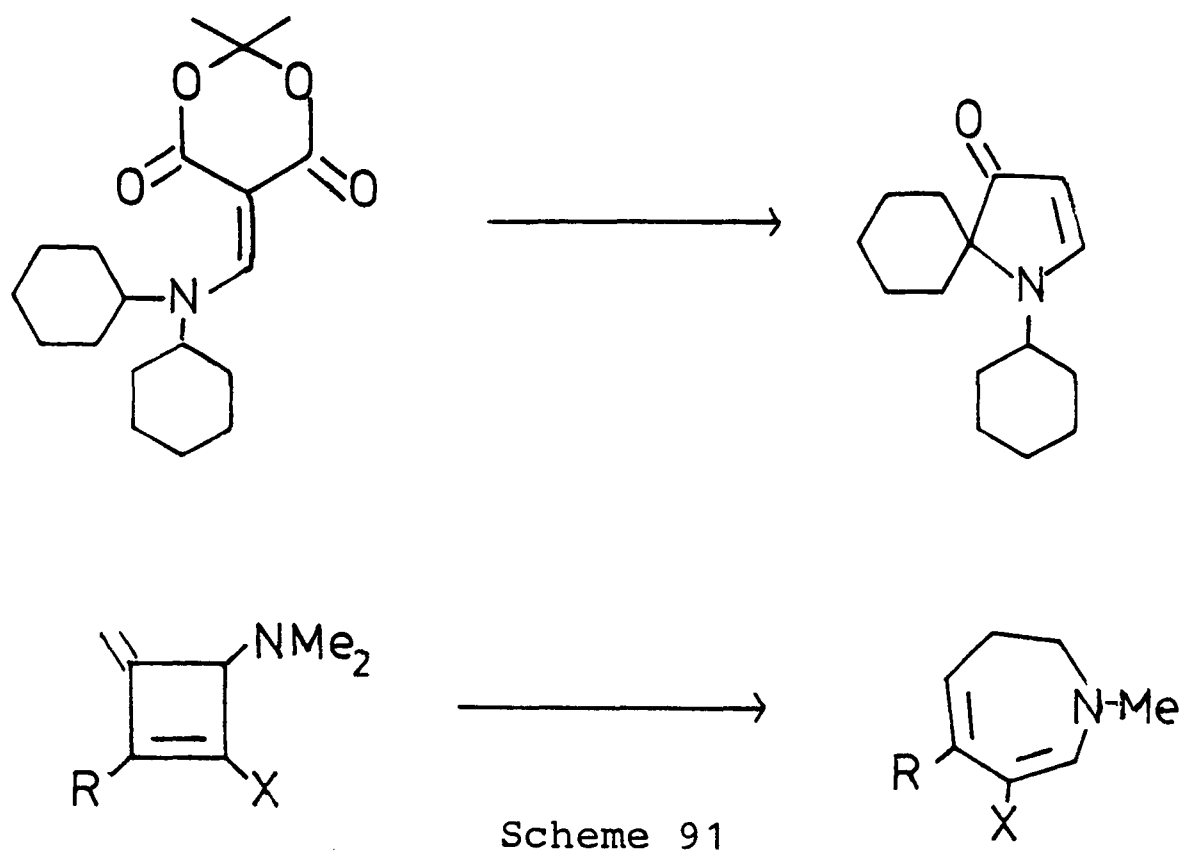
Ratios of Pyrroles Formed by Pyrolysis of (78) and (79)

	<u>Product Ratio</u>	<u>Selectivity</u>
Methyl : Ethyl	1:3	2:9 - $1^Y:2^Y$
Methyl : Isopropyl	2:3	2:9 - $1^Y:3^Y$

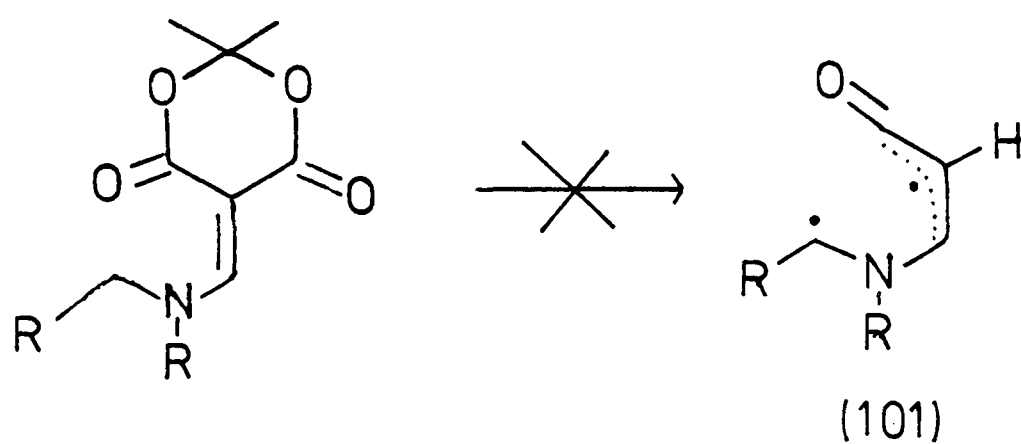
Table 3

The ratio for the radical intermediates would of course be expected to be greater for tertiary:primary than for secondary:primary. The steric hindrance of the bulky isopropyl group may be able to account for the smaller ratio.

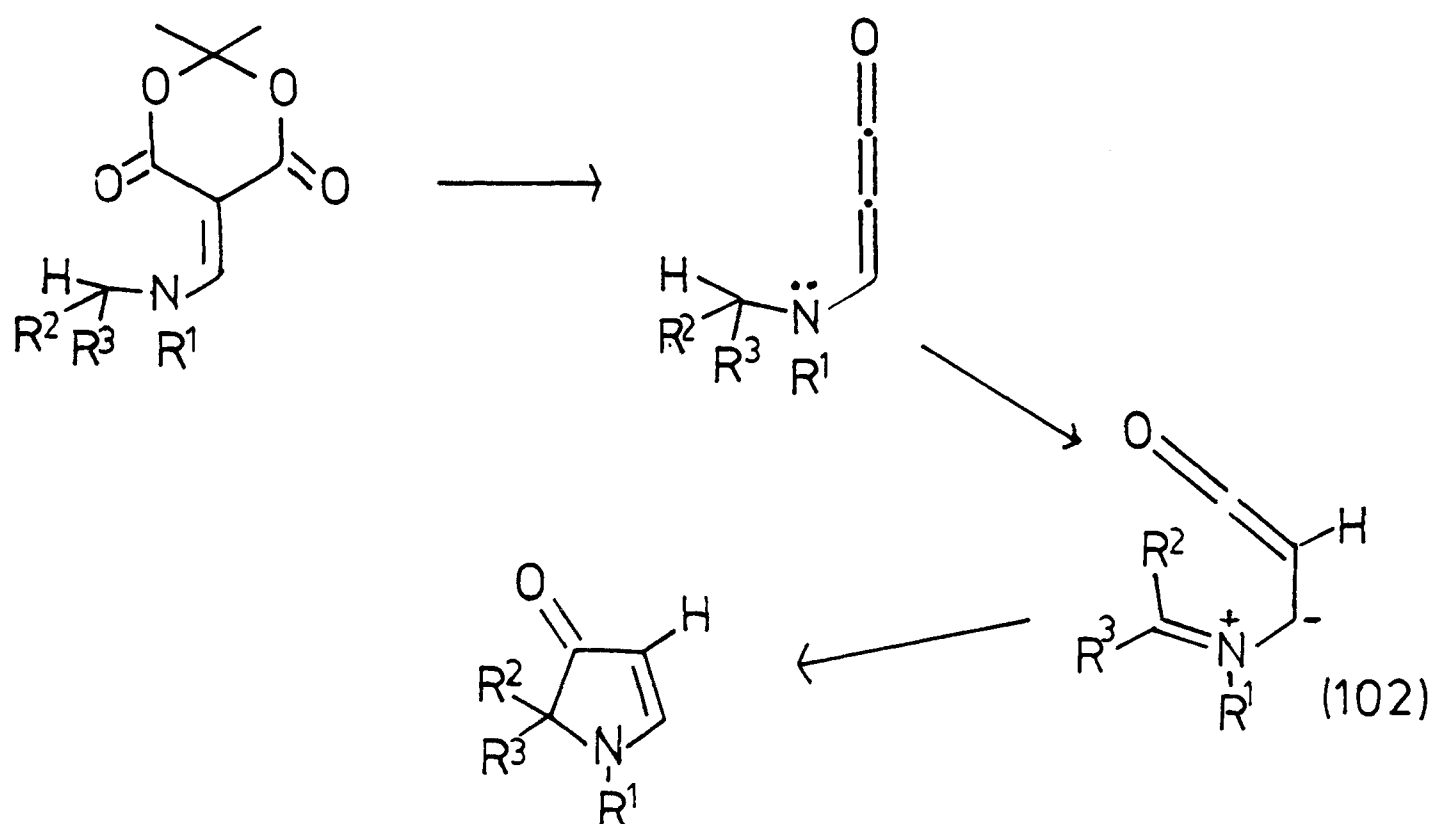
It is necessary to consider however just how much differential selectivity would be expected at 800°C. For comparison, it has been shown by Crow and McNab¹¹⁸ that for arylcarbenes, primary:secondary:tertiary selectivity at 500°C (0.01 Torr) is 1:4:9. However it may be that selectivity is reduced at higher temperatures. There are two other examples in the literature in which heterocyclic products are formed by thermal hydrogen transfer from a position adjacent to nitrogen (Scheme 91).^{114,119,120}



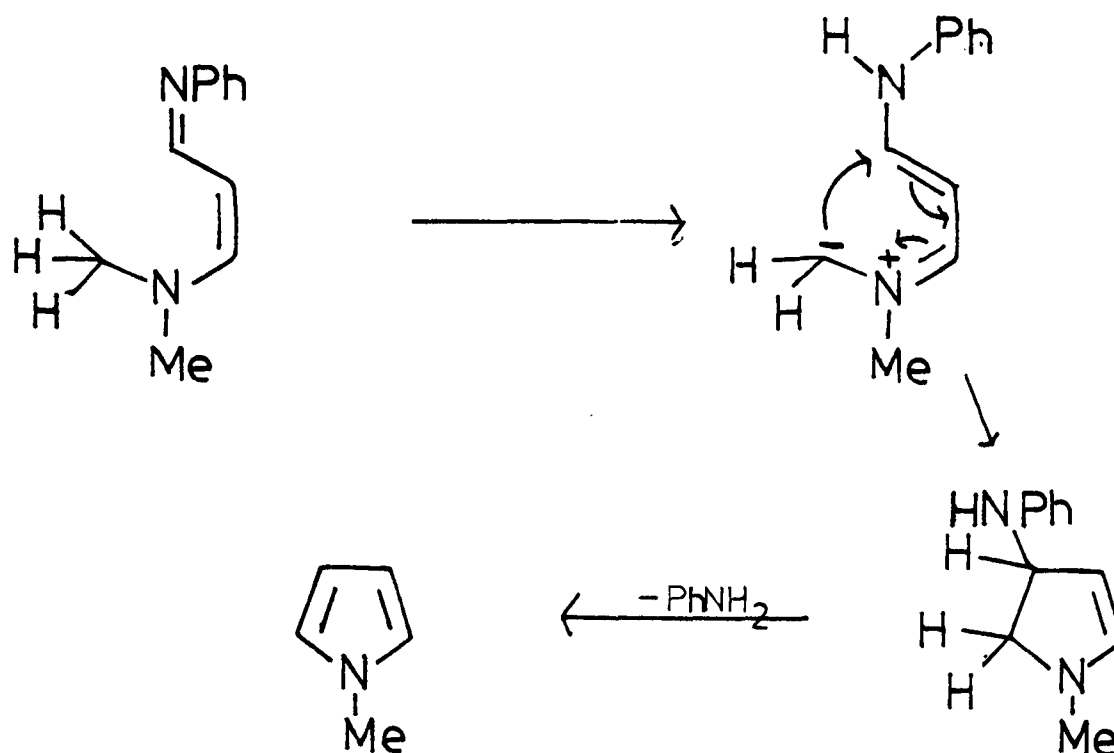
The mechanism of the formation of 1,2-dihydropyrrol-3-ones by pyrolysis of aminomethylene Meldrum's acid derivatives has been shown to be an intramolecular stepwise process.¹¹⁹ This reaction is better suited for more detailed study, since the final product is formed without the complication of subsequent aromatisation steps, which also destroy stereochemical information at the reaction site. It was shown that the hydrogen transfer step forms an intermediate, which has sufficient lifetime to undergo some C-N bond rotation prior to its collapse to the pyrrolone. However, a diradical structure (101) (Scheme 92) for this intermediate may be excluded as competitive experiments showed no clear pattern in primary:secondary:tertiary selectivity.

Scheme 92

An alternative 1,3-dipole mechanism is proposed¹¹⁹ for which the hydrogen shift to give the azomethine ylid (102) may be a six-electron electrocyclic process.

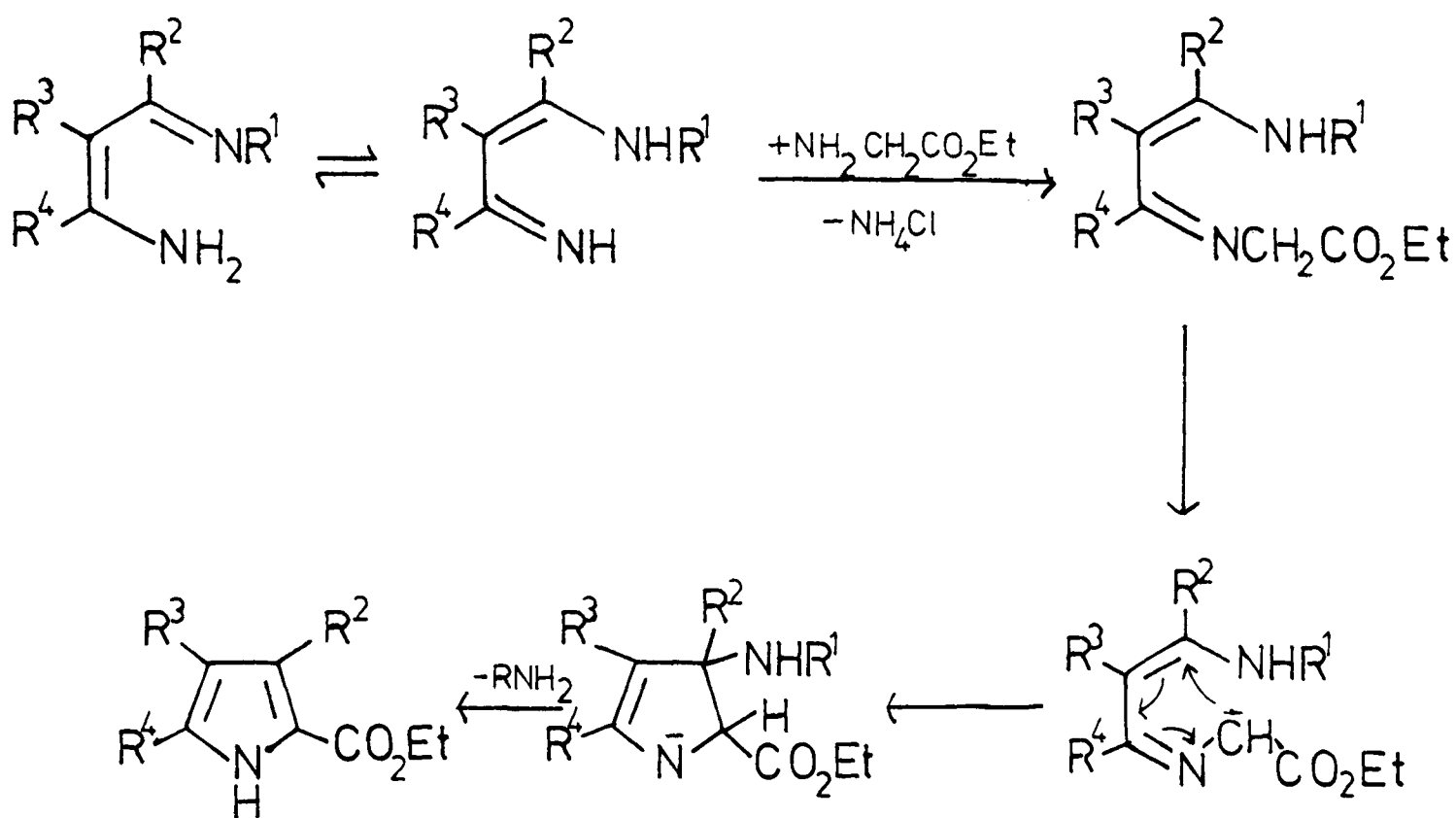
Scheme 93

If this mechanism is applicable to pyrrole formation then it would be as shown in Scheme 94.



Scheme 94

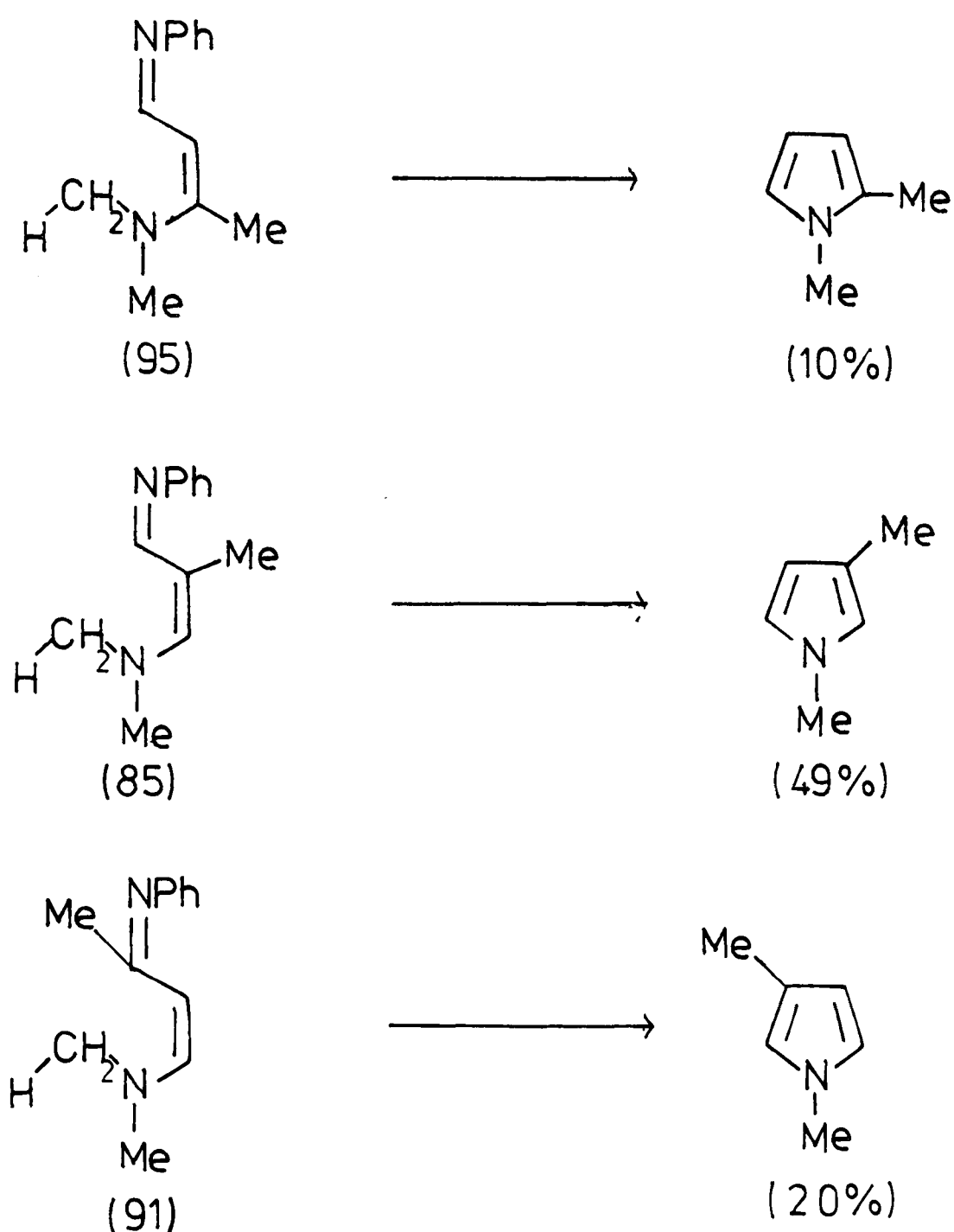
Another example of the cyclisation of 1,5-diazapentadienes to give pyrroles is known. Barluenga¹²¹ reports that the formation of heterocycles can be explained in terms of exchange reactions followed by deprotonation and electrocyclic closure.



Scheme 95

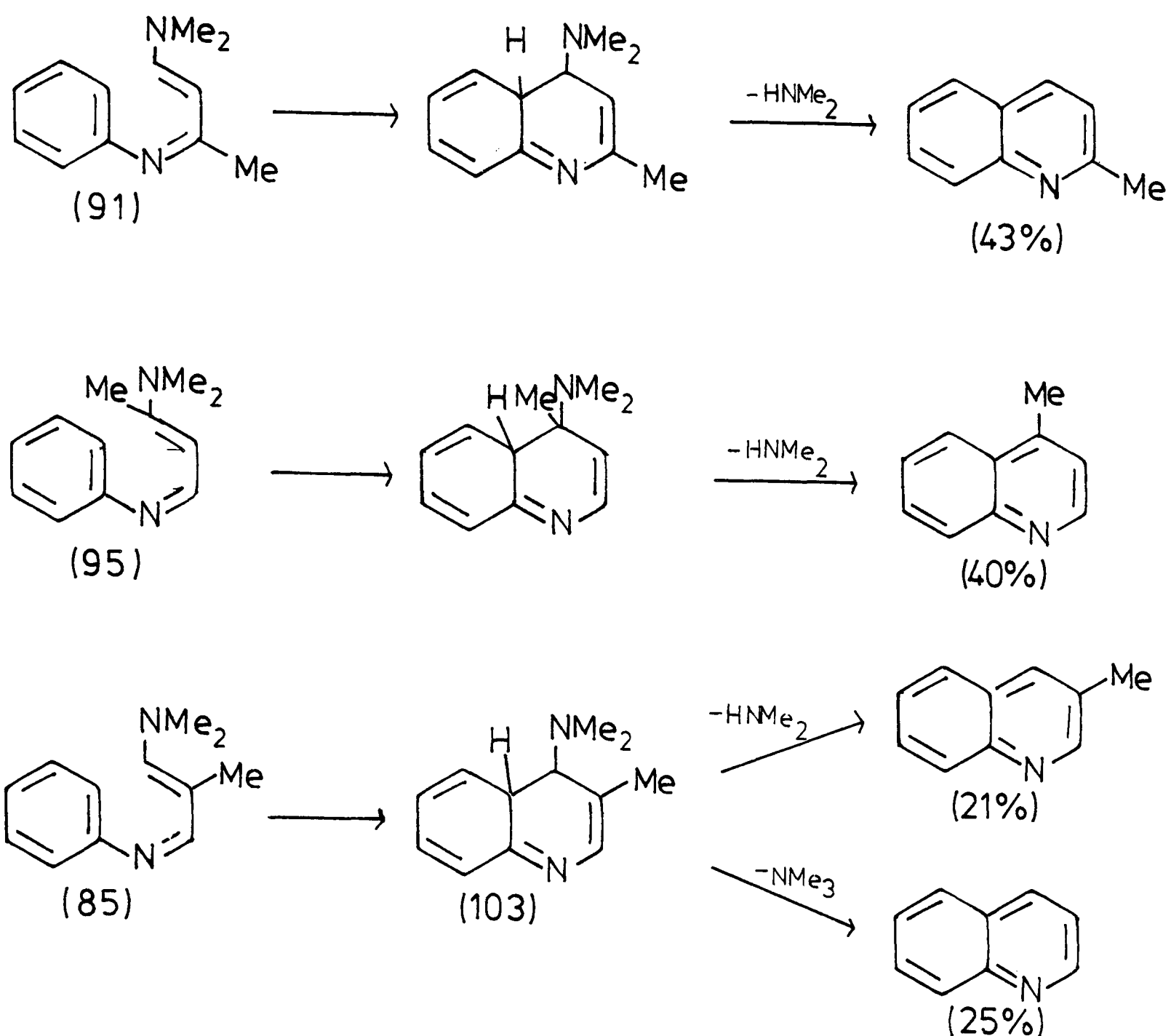
In Scheme 95, the heterocyclisation can be explained by an exchange reaction between the amino group of the glycine and the imino group present in one of the tautomer forms of the azabutadiene. The methylene group adjacent to the ester is activated to deprotonation under basic conditions which leads to azapentadienyl anions which can undergo an electrocyclic closure giving 1*H*-pyrrole-2-carboxylates.

When methyl groups were placed in various positions on the carbon chain of the diazapentadiene, the results were consistent with the diradical mechanism, giving the appropriate pyrroles (Scheme 96).



Scheme 96

The major difference for these methyl labelled diazapentadienes compared with the parent diazapentadiene on pyrolysis was that the yields of the quinolines formed were much higher with the methyl group present on the carbon chain than without as in the parent compound.

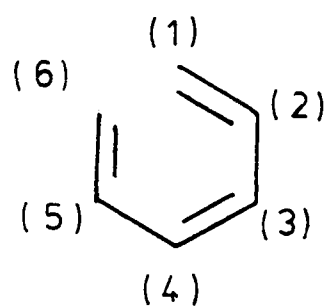


Scheme 97

Why should a methyl group on the carbon chain increase the yields of the quinolines?

The increase in the relative quinoline yields (Table 4) could either be due to an increase in the rate of electrocyclisation or else due to retardation of the hydrogen transfer process which leads to pyrroles. Whatever the mechanism of the hydrogen transfer step, it is difficult to see how this could be similarly hindered by methyl groups at different sites of the carbon chain, therefore acceleration of the quinoline formation seems more likely.

Relative Amounts of Quinolines : Pyrroles in 1,5-Diazapentadienes



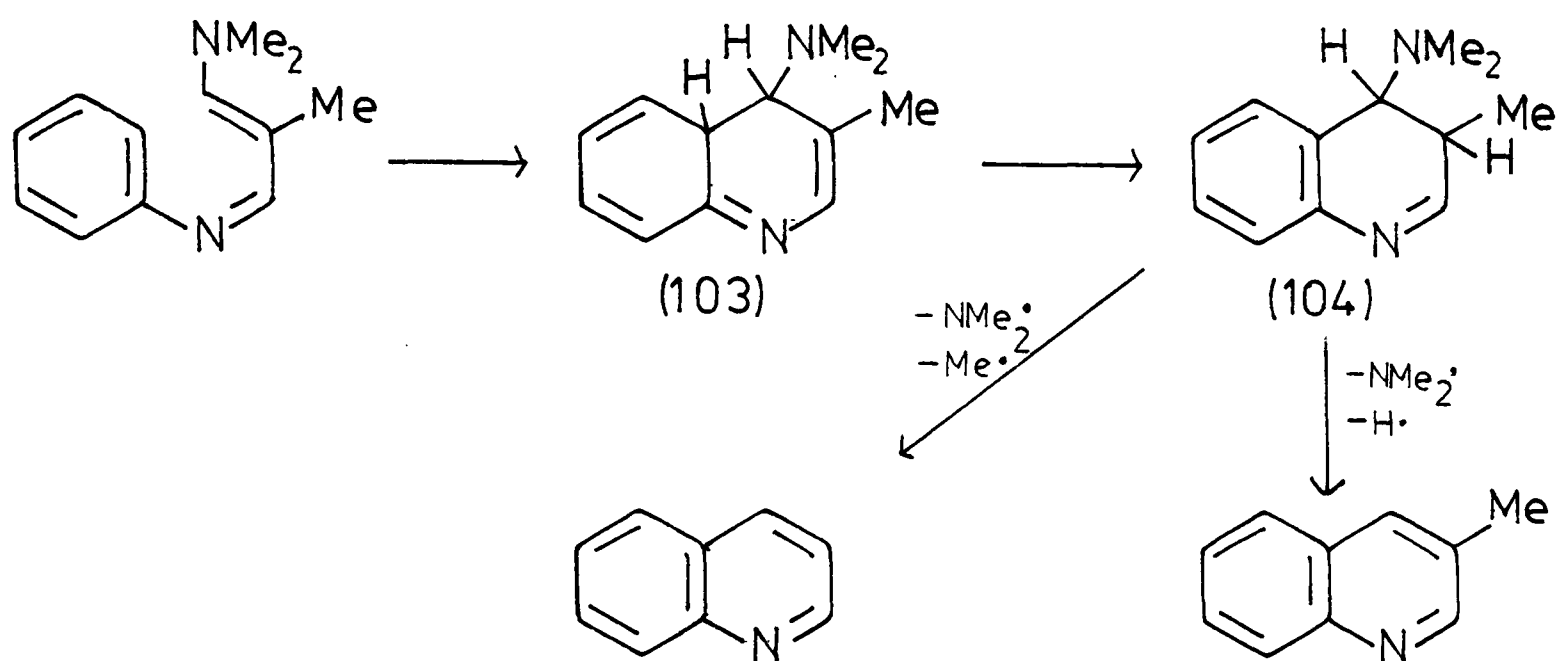
STARTING MATERIAL	POSITION OF METHYL ON HEXATRIENE	TOTAL QUINOLINES : TOTAL PYRROLES
(67)	-	0.23 : 1
(95)	1	4.0 : 1
(85)	2	0.94 : 1
(91)	3	2.15 : 1

TABLE 4

The effect of methyl groups at various sites on the thermal cyclisation of simple 1,3,5-trienes has been investigated kinetically but the data is incomplete.¹²² In general, substituents at the 2- and 3-positions of the triene produce a modest acceleration due to steric effects raising the energy of

the ground state.^{123,124} Groups at the 1 position display similar behaviour, though at a reduced level due to steric retardation.¹²⁵ In agreement with this an acceleration was found at all three positions in our examples (Table 4) though, unexpectedly, the major effect was found for methyl substitution at the 1-position.

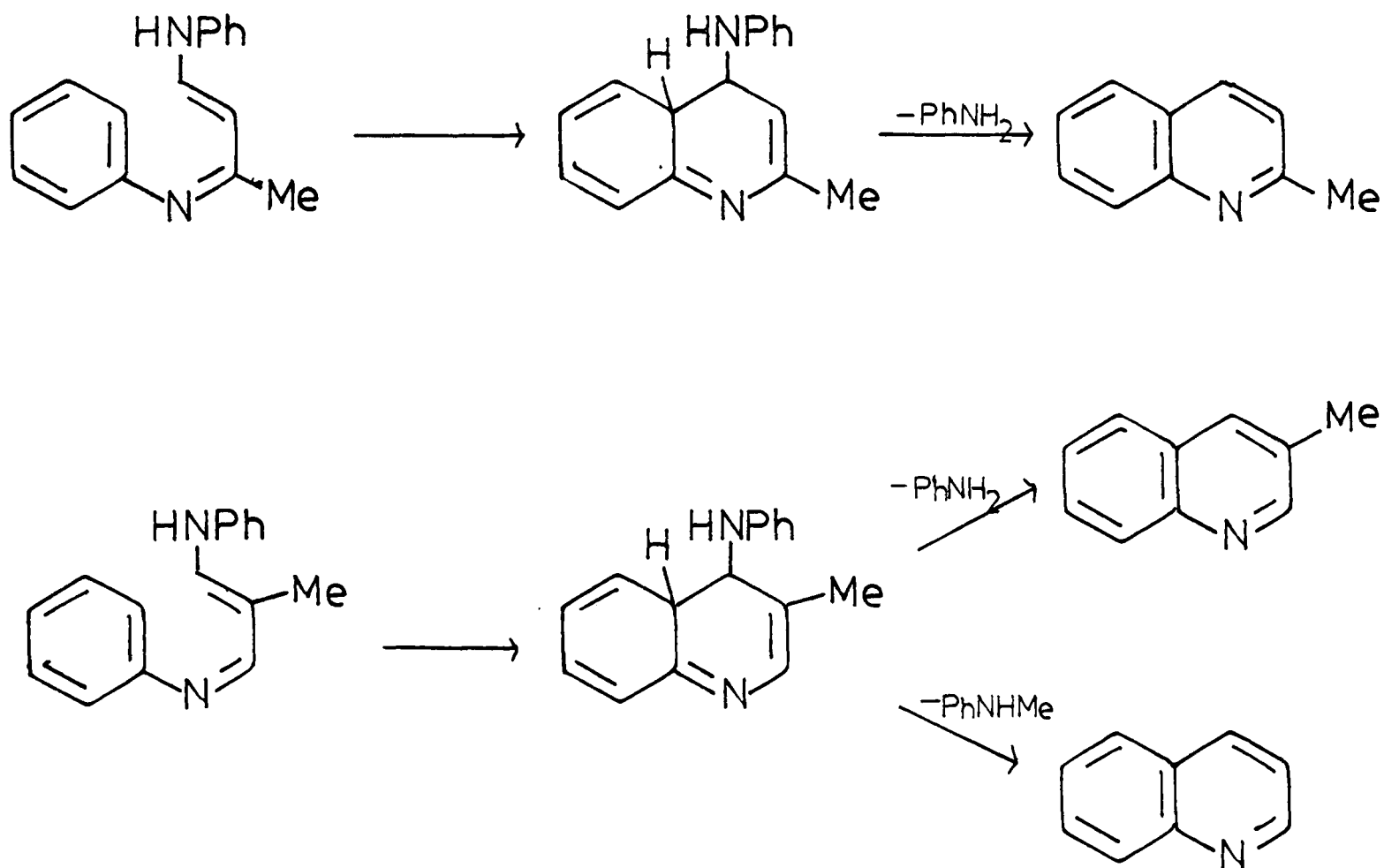
Scheme 97 shows how the appropriate methyl quinolines were obtained from the concerted electrocyclic reaction as expected. However, 5-phenyl-1,1,3-trimethyl-1,5-diazapentadiene (91) also gave quinoline itself unlike the other two. It is unlikely that direct cleavage of the vinyl methyl group from (103) could take place, though radical cleavage of methyl groups from sp^3 hybridised carbons is well known (cf. page 69). An intermediate with the structural requirement could be formed from (103) by an allowed 1,5-hydrogen shift (Scheme 98).



Scheme 98

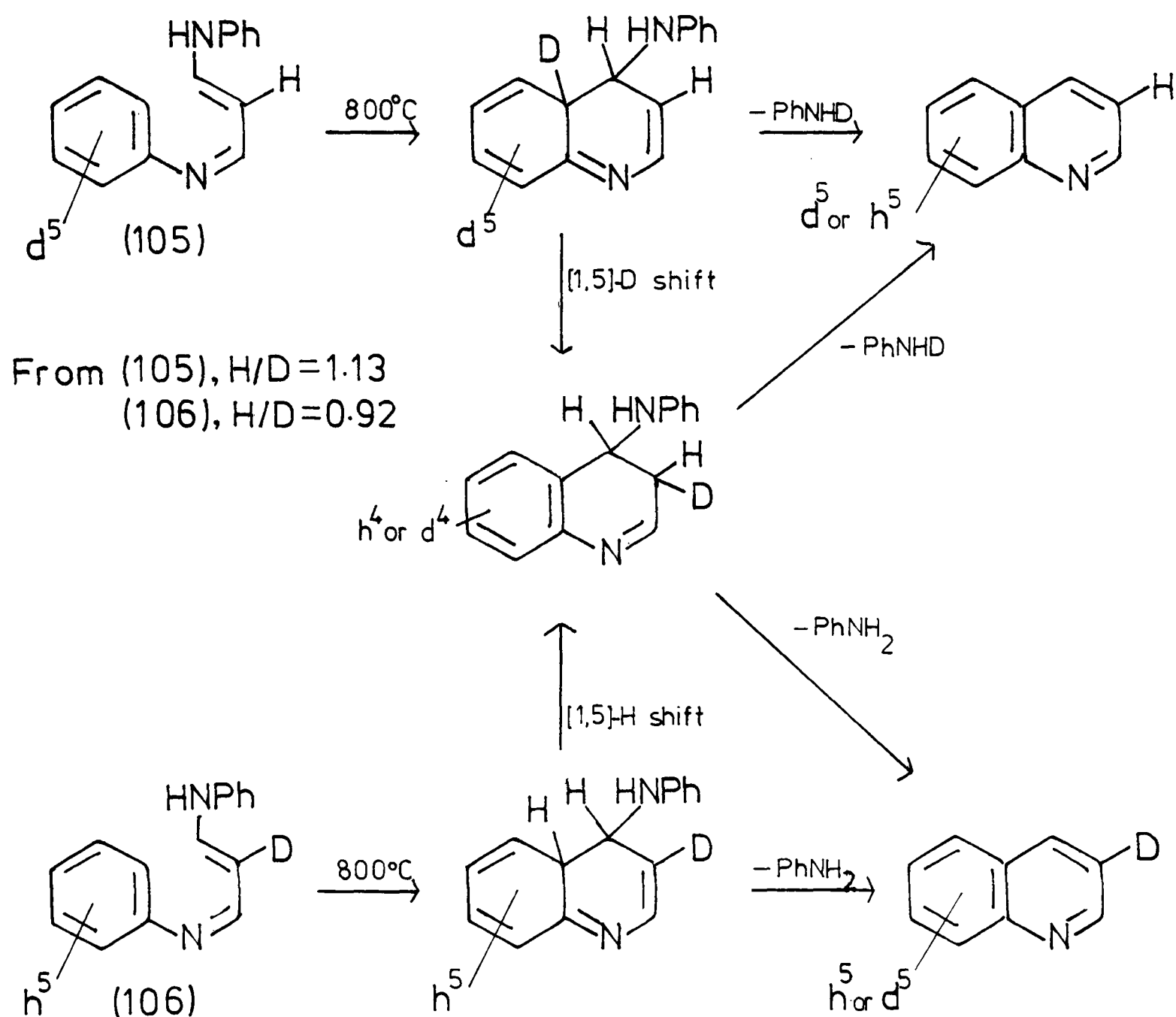
In the resultant (104) there is then competition between the hydrogen and the methyl to see which acts as a leaving group. However, in the 2- and 4-methyl labelled compounds (95) and (85), the methyl group would not be affected by a 1,5-shift and therefore quinoline is not formed to any real extent.

The pyrolysis of 2- and 3-methyl labelled 1,5-diphenyl-1,5-diazapentadienes confirmed the proposed mechanisms by giving only various quinolines⁶¹ (Scheme 99). No pyrroles were formed due to the fact that there was no hydrogen available to undergo an intramolecular transfer. Again, only the 3-methyl labelled compound formed quinoline to any extent, after a 1,5-shift placed the hydrogen atom and methyl group on the same carbon atom. Conversely, since sigmatropic shifts of methyl groups are generally slow, it is not surprising that pyrolysis of the di-*o*-tolyl compound (96) gave no 3-methyl quinoline.



Scheme 99

To confirm that a 1,5-shift did actually take place in the parent diazapentadiene and was not brought about by the presence of a methyl group, the appropriate deuteriated compounds were prepared and pyrolysed. As expected, quinoline with a deuterium atom incorporated in the three position was obtained by pyrolysis of the $[^2\text{H}_{10}]1,5\text{-diphenyl-1,5-diazapentadiene}$ (105) as shown by ^2H and ^1H n.m.r. spectroscopy.

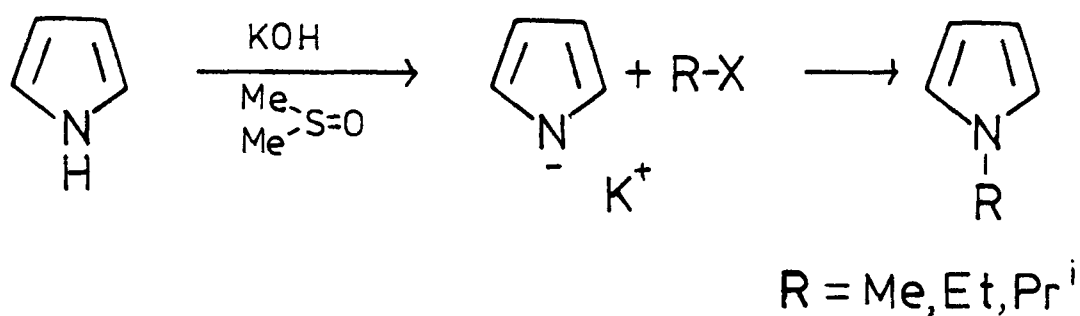


The H/D ratio from the pyrolysis of (105) was found to be 1.13 and from the pyrolysis of (106) it was 0.92. The ratios obtained are only approximate but are probably accurate to about 10%. Whether or not the fact that (105) has a ratio >1 and (106) has a ratio <1 indicates a slight leakage through to the product without undergoing a 1,5-shift is uncertain. It could be that the reaction goes completely *via* a 1,5-shift and the ratios obtained are close enough to one within experimental error. What is certain is that the rate determining step must either be the cyclisation step or else the loss of the anilino radical as the rate determining step does not involve transfer of H or D. This is clear due to the fact that no significant isotope effect is observed. Isotope effects are observed under flash vacuum pyrolysis conditions. For example, pyrolysis of di-trans-*o*-deuteriocinnamyl oxalate at 570°C indicated an isotope effect $\frac{k_H}{k_D}$ of 2.92.¹²⁵ At 800°C, the isotope effect $\frac{k_H}{k_D} \sim 1.4$ and it is obvious from the ratio that even allowing for experimental error no isotope effect is observed.¹²⁵

III PREPARATION OF ALKYLPIRROLES FOR COMPARISON WITH PYROLYSATES

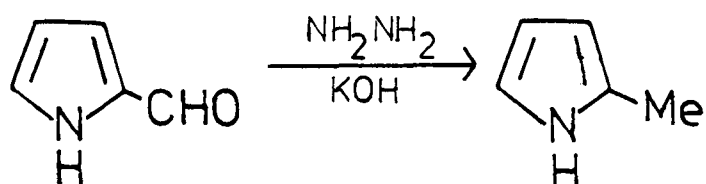
The pyrroles obtained in the pyrolysates of the various diazapentadienes were identified by comparison with authentic samples - with the exception of 1,3-dimethylpyrrole. This compound would be derived from 3-methylpyrrole which is not readily available.¹²⁷

1-Alkylpyrroles were prepared as shown in Scheme 101.¹²⁸



Scheme 101

The potassium salt of the pyrrole was formed first by interaction with powdered potassium hydroxide in dimethyl sulphoxide at room temperature. Alkylation was then achieved without isolation of the potassium salts by addition of an excess of the appropriate alkyl halide, also at room temperature.



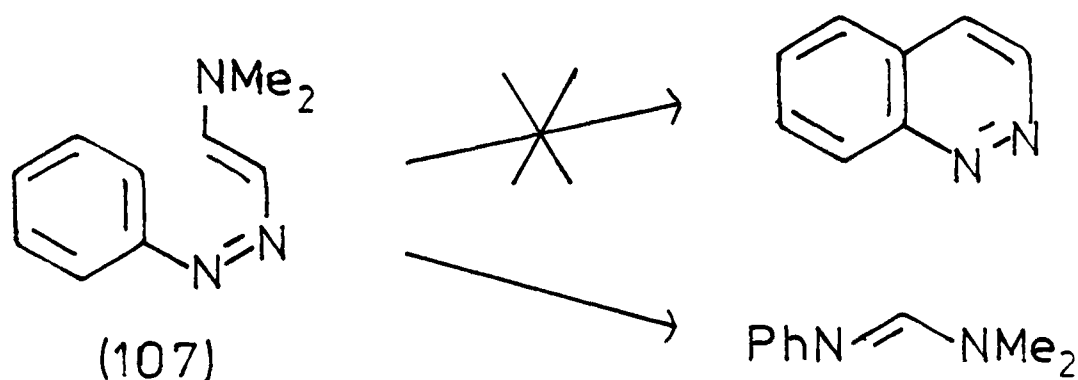
Scheme 102

2-Methylpyrrole¹²⁸ was prepared by reduction of pyrrole-2-aldehyde using the Huang Minlon¹²⁹ modification of the Wolff-Kishner reaction. The pyrrole-2-aldehyde was added to a mixture of hydrazine hydrate and potassium hydroxide in diethylene glycol, as shown in Scheme 102. 2-Methylpyrrole was separated from the mixture and alkylated as above to give 1,2-dimethylpyrrole and 1-ethyl-2-methylpyrrole.

B. Preparation and Pyrolysis of Various Hetero-2-azadienes

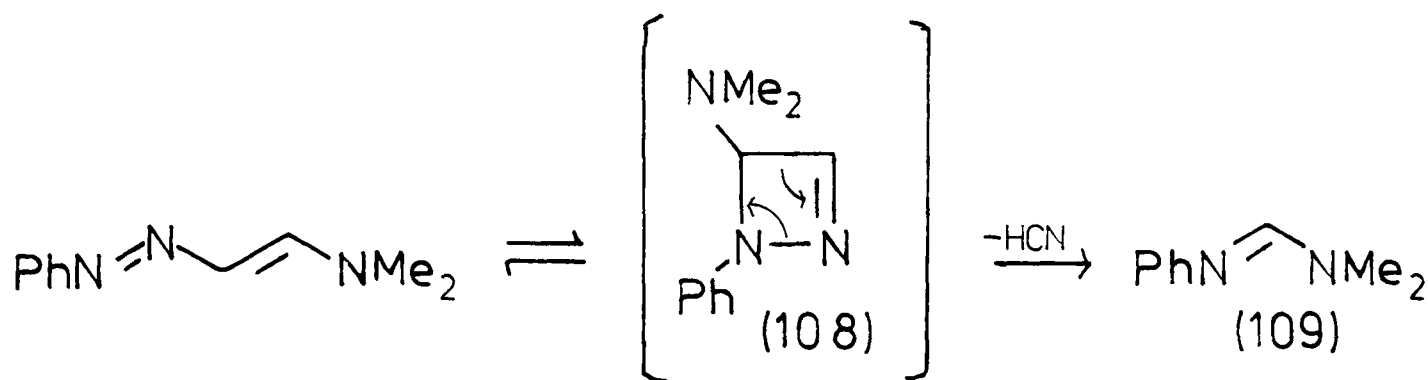
I Introduction

Flash vacuum pyrolysis of 1,5-diaryl-1,2,5-triazapentadienes has been shown to yield quinoxalines^{64,66} (Scheme 80). Yet, an attempt to prepare cinnoline by a related procedure by pyrolysing the 5,5-dimethyl derivative (107) found a completely different reaction taking place⁹⁸ (Scheme 103).



Scheme 103

The reaction appears to proceed through a diazetine intermediate (108) which breaks down with loss of HCN to give 3,3-dimethyl-1-phenyl-1,3-diazapropene (109) (Scheme 104).



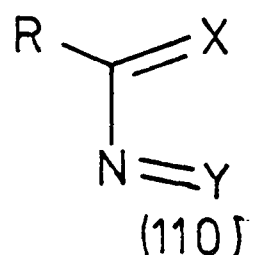
Scheme 104

There is now considerable support in the literature for this type of mechanism, as was discussed in the introduction

(section III, part 2).

It was of interest to discover the generality of this reaction and whether or not it is followed by other azoalkenes and compounds of the same general structure.

Heteroazadienes:



Compound No.	X	Y	R
107	CH-NMe ₂	N-Ph	H
111	CH-Ph	N-Ph	H
112	CH-pClPh	N-Ph	H
113	CH-Ph	N-oClPh	H
114	CHCO ₂ Me	N-Ph	Me
115	CHCO ₂ Et	N-Ph	Me
116	O	CH-NMe ₂	Me
117	O	CH-NMe ₂	Et
118	O	CH-NMe ₂	Ph
119	S	CH-NMe ₂	Ph
120	O	C(Ph) ₂	Ph
121	O	C(Ph) ₂	p-tolyl
122	O	N-Ph	Ph
123	O	N-Ph	p-tolyl
124	O	N-Ph	o-methoxyphenyl
125	NPh	CH-NMe ₂	methyl

Table 5

To fulfill this objective, the basic azoalkene type molecule (110) was altered to find how far it could be contorted and yet still undergo the same reaction. A comprehensive literature search was undertaken and played a decisive role in choosing compounds worthy of investigation.

The literature search revealed that some simple compounds of the required general structure were unknown, some were known but unstable and others were known but had already been pyrolysed (cf. introduction, part III, section 2). The remaining compounds, many of which were subsequently pyrolysed, were generally found only to be stable with Y as an *N*-phenyl group or else with a dimethylamine group attached to a methylene carbon.

The 5,5-dimethyl-1-phenyl-1,2,5-triazapentadiene (107) had a dimethylamino group attached to a carbon at position X. Replacement of this group with either a phenyl or *para* chloro phenyl was able to show whether or not a less electron donating substituent at that position had any effect on the reaction. Compounds (111) and (112) were known, relatively stable and were therefore prepared. Compound (113) was also prepared; this had a chloro substituent on the *N*-phenyl group at position Y and therefore showed whether or not altering the electronegativity at this site affected the course of the reaction. Compounds (114) and (115) were relatively easy to prepare and showed the effect, if any, of an electron withdrawing ester group at position X.

The basic azoalkene structure (110) was altered considerably more when the carbon group at position X was replaced by an oxygen or sulphur atom and a methylene carbon with a

dimethylamino group attached at position Y in compounds (116), (117), (118) and (119).

The next logical progression would be the replacement of the dimethylamino group with a phenyl group. These compounds are known^{130,131} but are found to be particularly unstable.¹³² The explanation in the literature for this instability is assigned to the strong polarisation of electrons¹³³ and the need for electronegative substituents on the methylene carbon to act as a counterbalance.^{134,135} This explanation is not an adequate one as compounds (116), (117), (118) and (119) each have a dimethylamino group on the methylene carbon and yet are relatively stable.

The closest, stable, analogous compounds (120) and (121) had two phenyl groups rather than just one, attached to the methylene carbon, although there were problems with these compounds as they tended to hydrolyse to the amide. There were also problems with the characterisation as, with only aromatic protons present, ¹H n.m.r. spectroscopy does not yield a great deal of information.

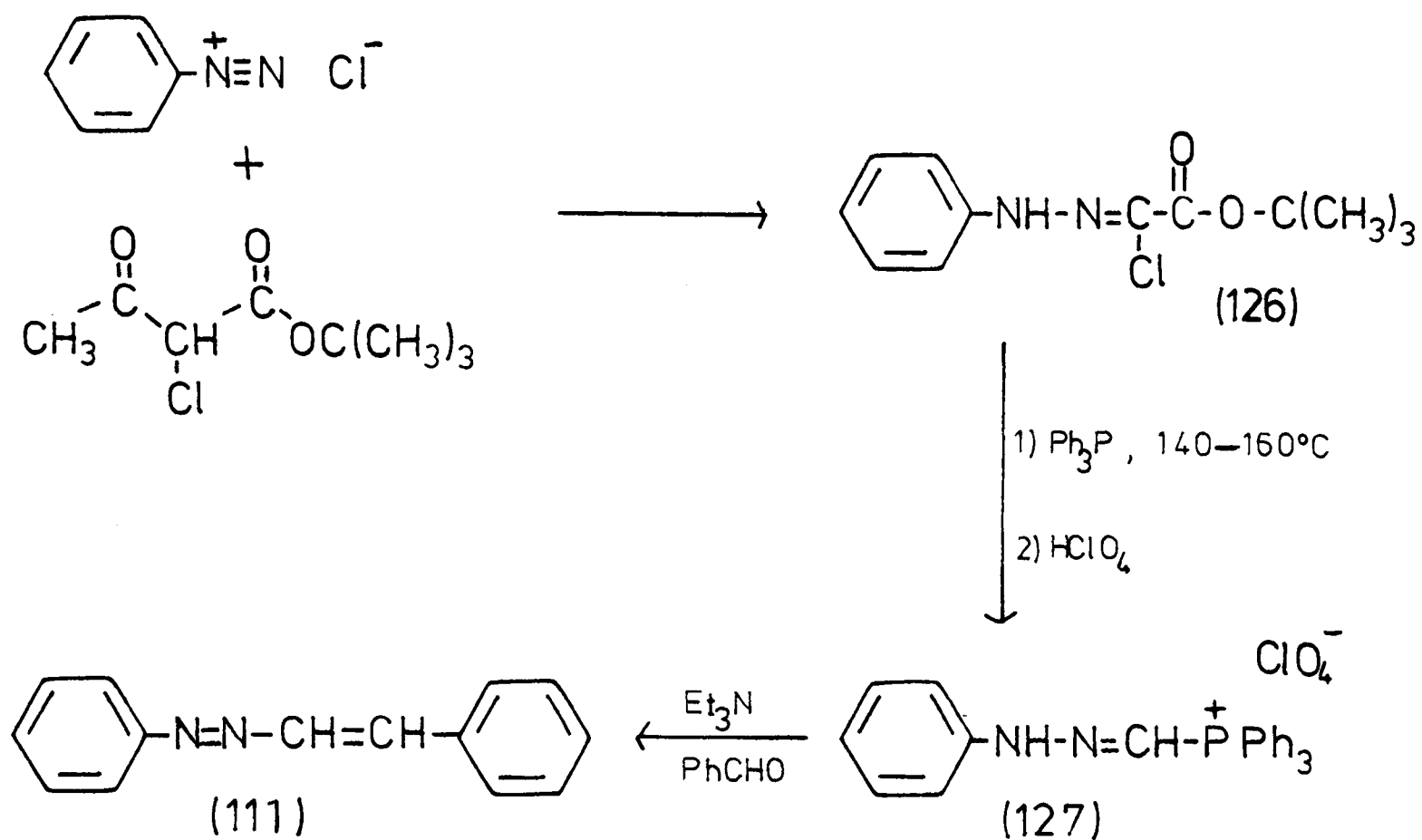
Similarly, replacement of the methylene carbon and substituents by an *N*-phenyl group as in compounds (122), (123) and (124) also caused problems with characterisation, due to the presence of aromatic protons only. These compounds were easier to handle however.

The final hetero-2-azadiene to be prepared and pyrolysed was (125), which involved replacing the oxygen of compound (116) with an anilino group. This was of particular interest because (125) is also very like (91), the pyrolysis of which was discussed in the previous section. There would appear to

be three different reaction pathways for this compound to undergo on pyrolysis: 6π electrocyclisation with elimination, hydrogen transfer to give a diradical intermediate followed by elimination, or else *via* a four membered ring azetine intermediate as in Scheme 104.

II Preparation, Properties and Pyrolysis of 1,4-Diaryl-1,2-diazabutadienes

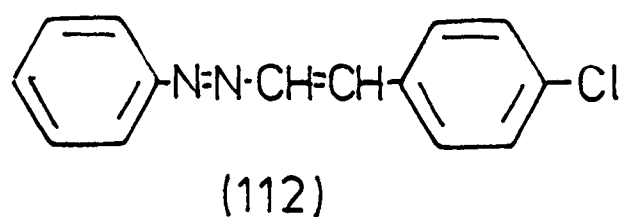
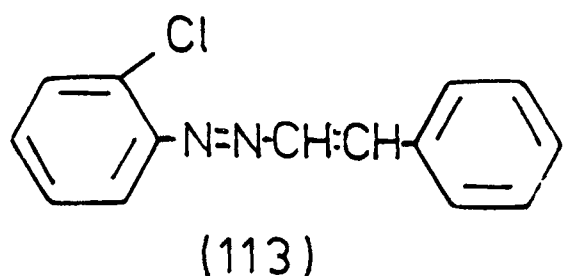
1,4-Diphenyl-1,2-diazabutadiene was prepared as shown in Scheme 105.



Scheme 105

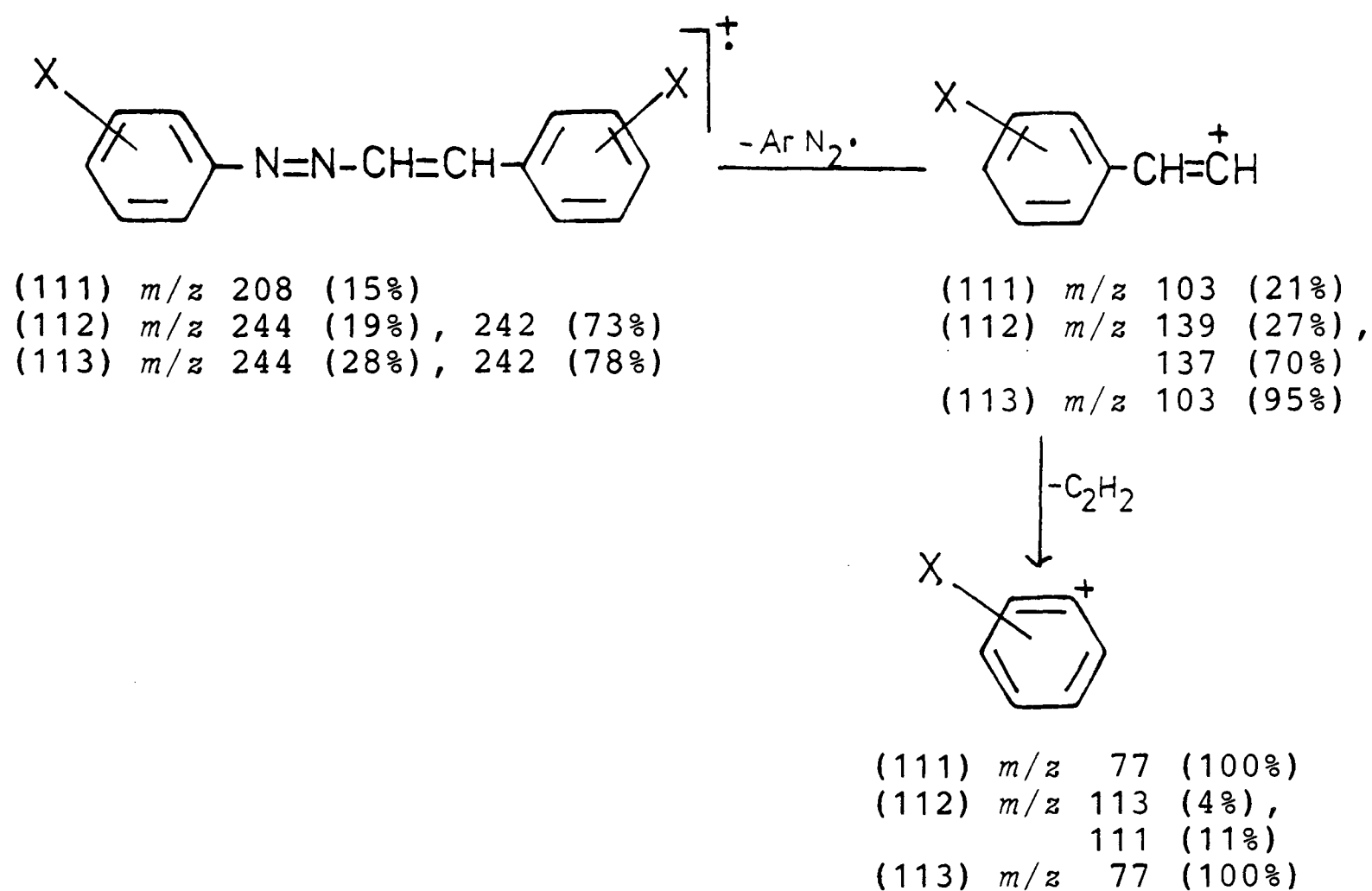
Chlorination of *t*-butylacetoacetate with sulphuryl chloride gave α -chloro-*t*-butylacetoacetate, from which *t*-butyl-1-chloropyruvate phenylhydrazone (126) was formed by reaction with benzene diazonium chloride. This in turn was treated with triphenylphosphine and perchloric acid to give formyl-triphenylphosphonium phenylhydrazone perchlorate (127). Treatment of the perchlorate salt with benzaldehyde in triethylamine produced the required 1,4-diphenyl-1,2-diazabutadiene (111).

Two other 1,4-diaryl-1,2-diazabutadienes were prepared using the same method. 1-(*o*-Chlorophenyl)-4-phenyl-1,2-diazabutadiene (113) used *o*-chloroaniline instead of aniline to prepare the diazonium salt and 1-phenyl-4-(*p*-chlorophenyl)-1,2-diazabutadiene (112) used *p*-chlorobenzaldehyde, in place of benzaldehyde, in the final step.



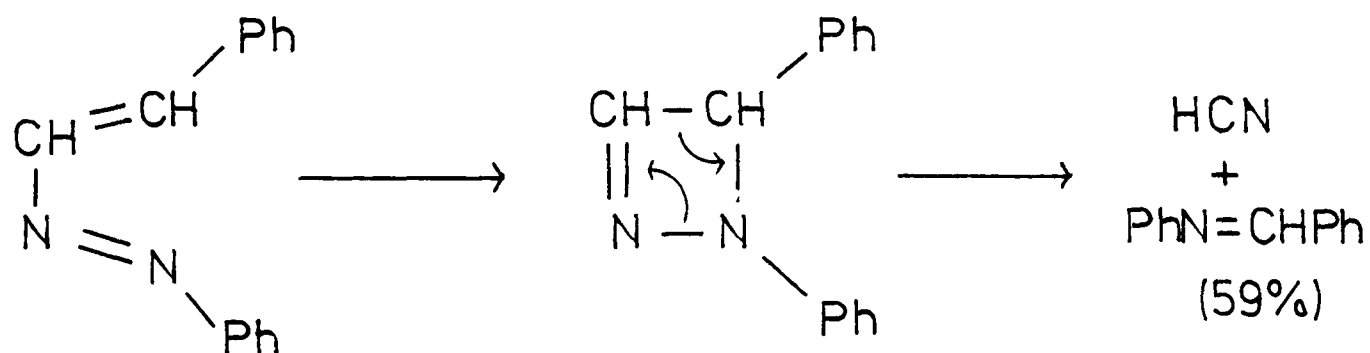
It is interesting to study the mass spectral fragmentation patterns of these 1,4-diaryl-1,2-diazabutadienes, to be able to compare their behaviour under electron impact with that on pyrolysis.

Unlike the 1,5-diazapentadienes discussed in part A, these diazabutadienes do not follow the same pathway, under electron impact and thermolysis conditions. They appear to fragment in the mass spectrometer *via* cleavage of the C-N bond of the azoalkene system (eg. 208→103), followed by loss of acetylene (eg. 103→77). The chloro substituent of compound (112) is still apparent after the cleavage of the C-N bond (m/z 139, 137).



Scheme 106

The mechanism for the reaction which takes place on pyrolysis of 1,4-diphenyl-1,2-diazabutadiene (111) at 650°C appears to be similar to that observed for the triazapentadiene (107) i.e. fragmentation *via* a diazetine intermediate.

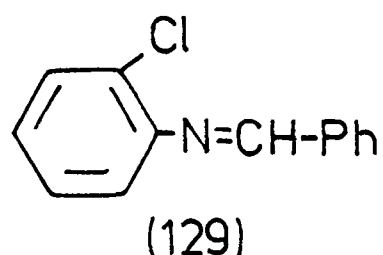
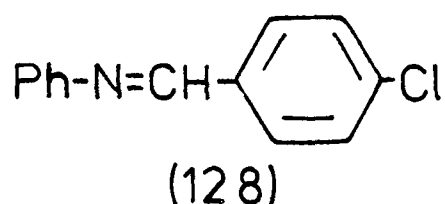


Scheme 107

Thus, incorporation of a less electron donating substituent at position X of the general azoalkene molecule has not altered the pathway, *via* the 4π electrocyclisation. Benzylidene aniline was shown by ^1H n.m.r. spectroscopy and g.c. to be the

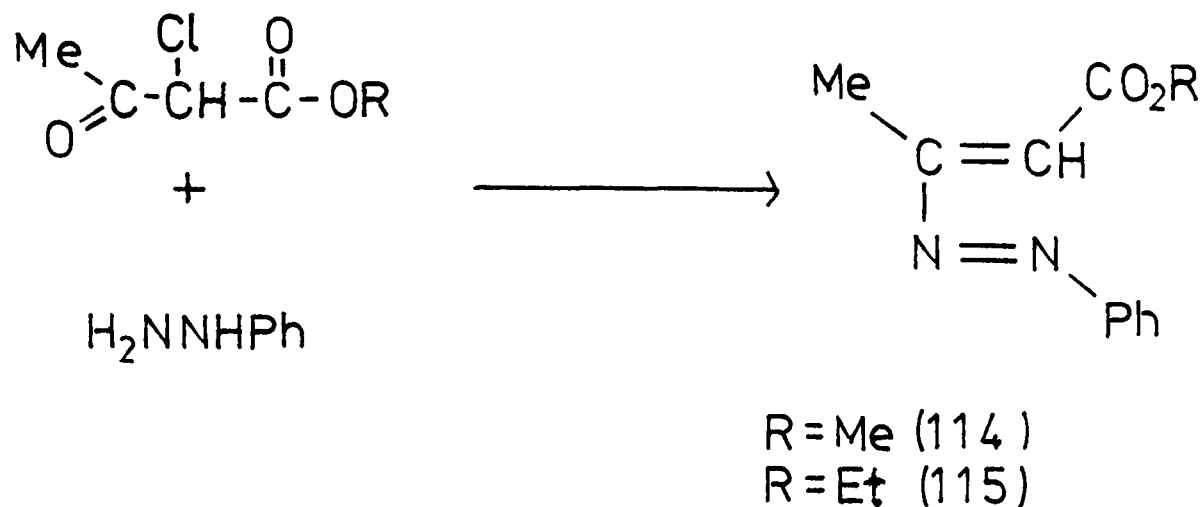
only significant product in the pyrolysate, therefore it was also possible to confirm its identification by melting point and mixed melting point with an authentic sample.

For the pyrolysis of the chloro substituted compounds (112) and (113) it was necessary to use the vertical furnace (as described on page 148), due to the decomposition of these compounds under prolonged exposure to high temperatures at the inlet to the horizontal furnace. In both examples, the compounds lost HCN to give the appropriately substituted benzylidene anilines (128) and (129), from (112) and (113) respectively.



This confirmed the intramolecular mechanism *via* the diazetine intermediate as no scrambling of the aryl groups took place.

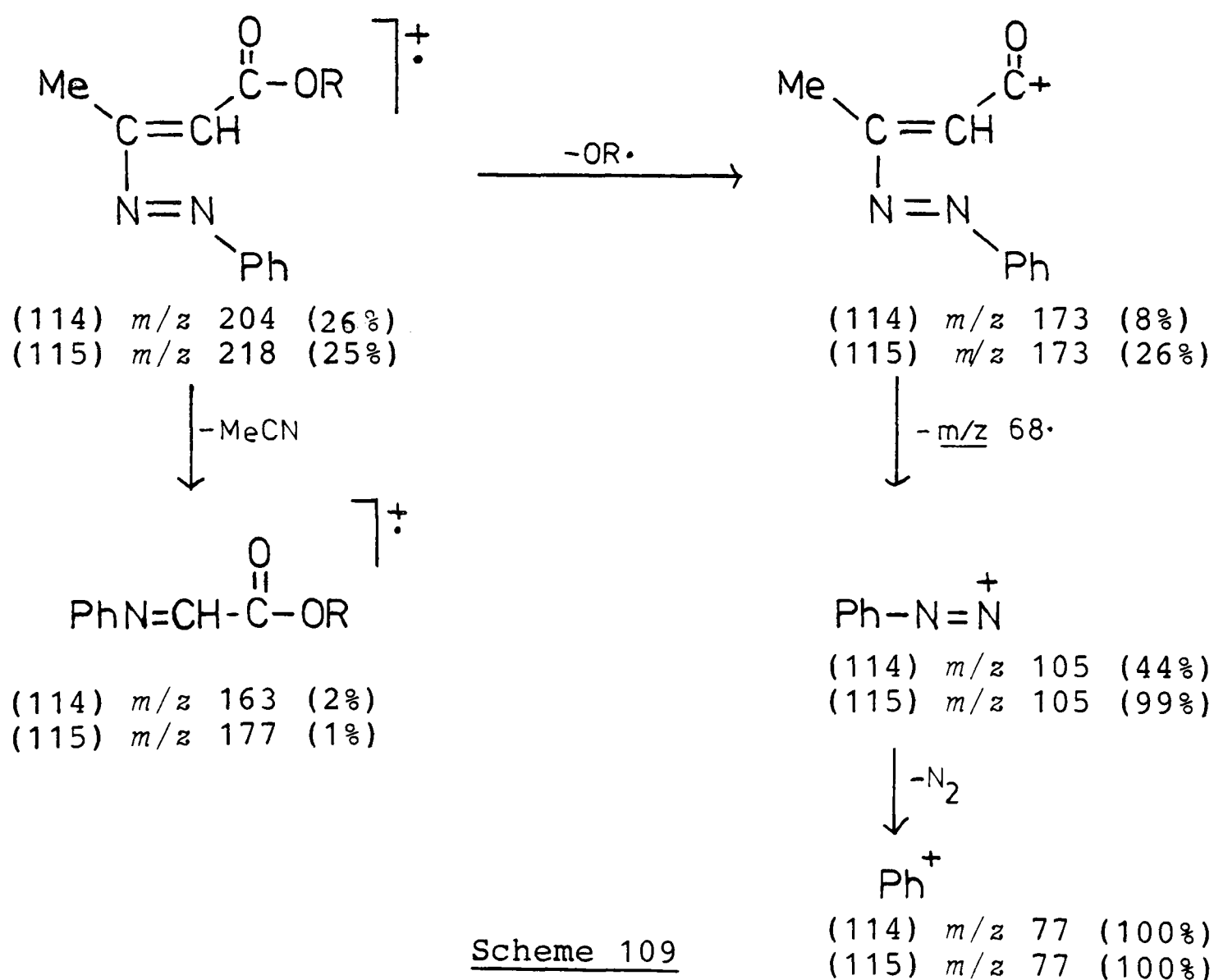
III Preparation, Properties and Pyrolysis of Alkyl-3-(phenylazo)but-2-enoates



Scheme 108

Methyl and ethyl 3-(phenylazo)but-2-enoates (114) and (115) respectively were prepared by reaction of the appropriate alkyl chloro^{aceto}acetate with phenylhydrazine as shown in Scheme 108.

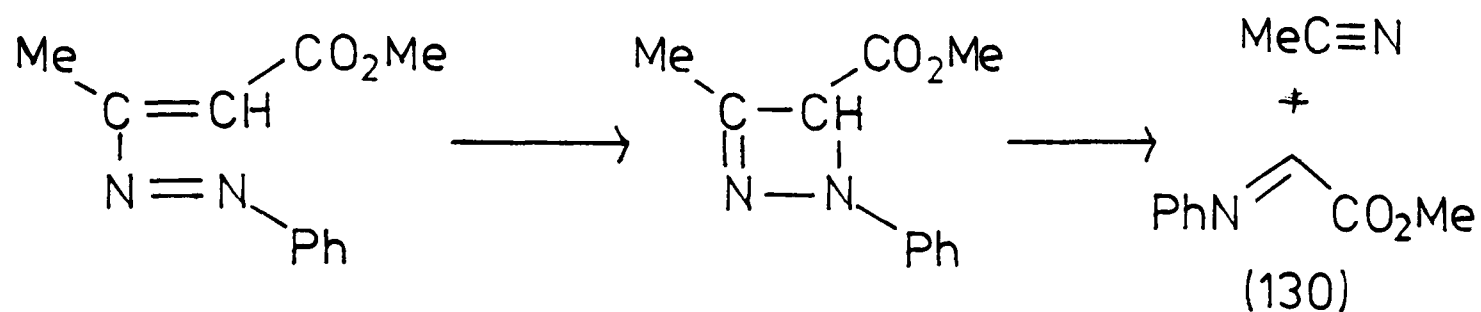
Examination of the mass spectra showed the breakdown patterns, on electron impact, to be as shown in Scheme 109.



Scheme 109

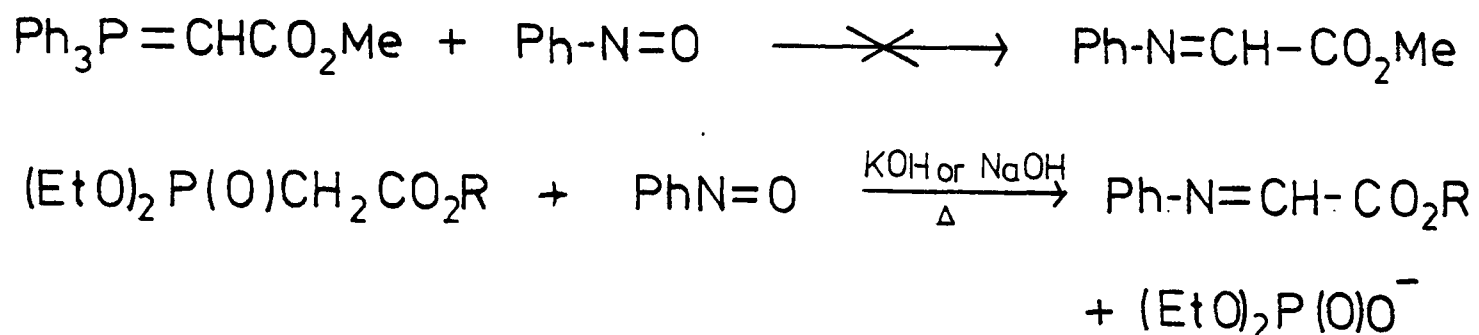
The major pathway involved fragmentation of the alkoxy group, followed by cleavage of the C-N bond of the azoalkene system (173→105) with subsequent loss of nitrogen (105→77). to give the phenyl cation (100%). There was little evidence for loss of alkyl cyanide from the parent ion with concomitant formation of alkyl glyoxylate (130), although small peaks were observed at 163 (2%) and 177 (1%) in the mass spectra, corresponding to the methyl and ethyl compound respectively.

Flash vacuum pyrolysis at 650°C (10^{-3} Torr) of methyl-3-(phenylazo)but-2-enoate (114) was found to be very different to previous pyrolyses as the pyrolysate was not clean and obviously was a mixture of a large number of compounds and polymeric materials. The gas chromatogram showed two main peaks to be present. The first peak was identified as aniline (m/z 93), the source of which is unclear, but probably involves high energy hydrogen atom capture. The second peak was tentatively identified as methyl glyoxylate anil (m/z 163), indicating again a route *via* a four-membered ring intermediate as shown in Scheme 110. It was not possible to obtain percentage yields for these products, but both were thought to be present in only trace amounts.



Scheme 110

Several attempts were made to prepare an authentic sample of methyl glyoxylate anil including a Wittig reaction of methyl(triphenylphosphoranylidene) acetate with nitrosobenzene, and a Wadsworth-Emmons modification of the Wittig reaction of the appropriate phosphonate with nitrosobenzene, using either potassium hydroxide or sodium hydride as base (Scheme 111).



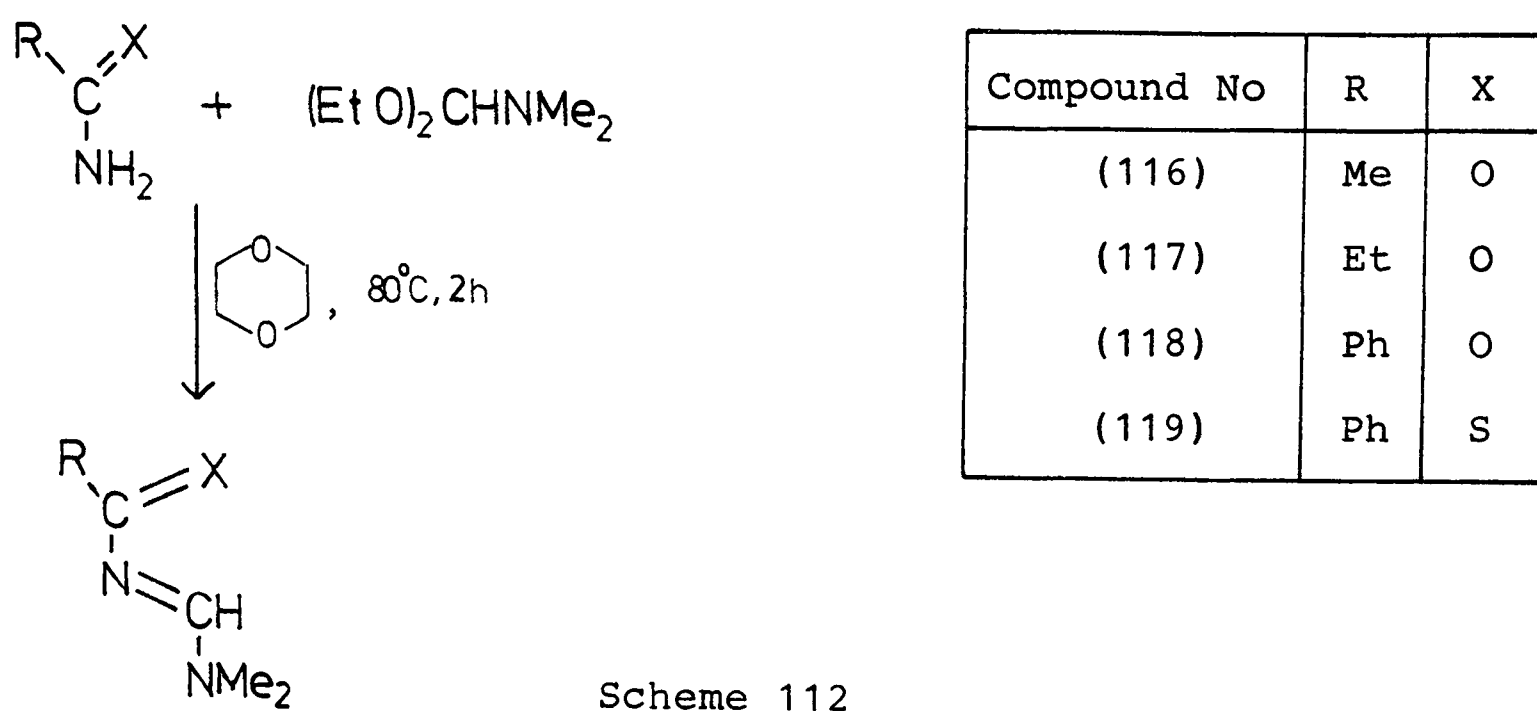
Scheme 111

Pyrolysis of the ethyl-3-(phenylazo)but-2-enoate under similar conditions was inconclusive. Ethyl esters generally breakdown on pyrolysis with loss of the ester linkage to give ethene (Scheme 1),¹² therefore complicating the study of the reaction under investigation.

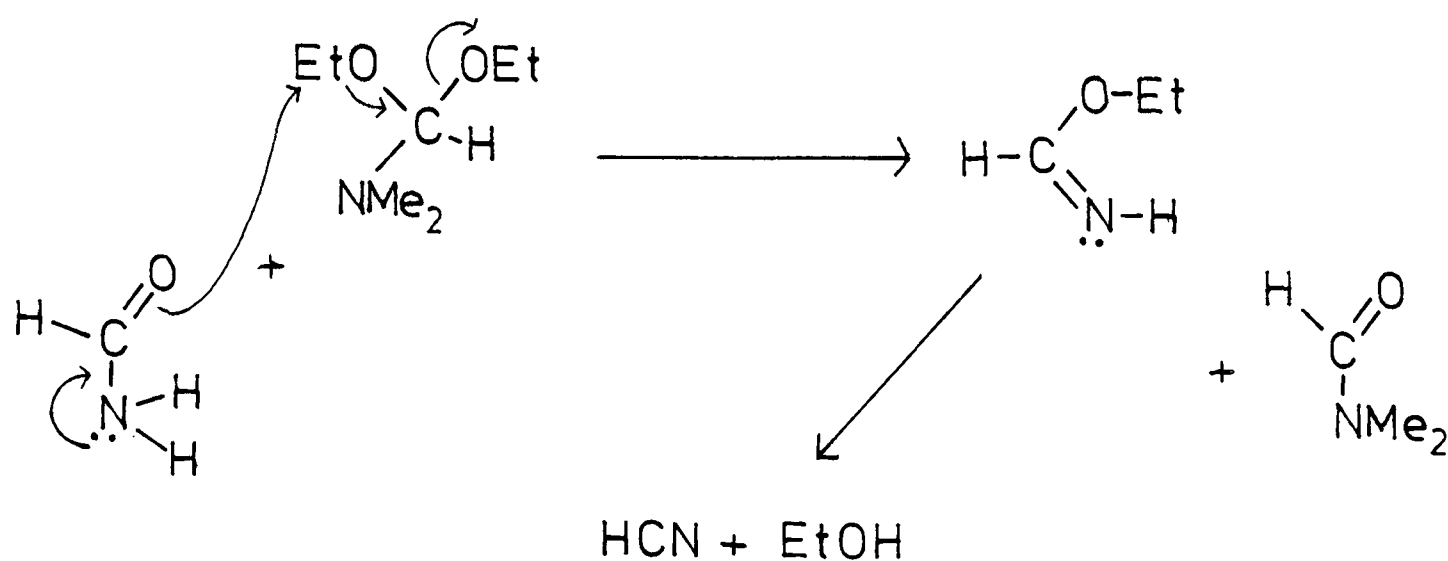
It is not clear therefore whether an electron withdrawing group at position X of the basic azoalkene (110) hinders reaction *via* the four membered ring intermediate or whether the complications mentioned above are due specifically to the special reactions of the ester function. It was therefore decided to replace the ester group by an oxygen or sulphur atom to find the effect of an electron withdrawing group at that position, in contrast to the strong and weak electron donating groups used in previous examples.

IV Preparation, Properties and Pyrolysis of 3-Dimethylamino-2-azaprop-2-en-1-ones

A variety of 3-dimethylamino-2-azaprop-2-en-1-ones were prepared by reacting the appropriate amide (or thioamide) with *N,N*-dimethylformamide diethylacetal as shown in Scheme 112.



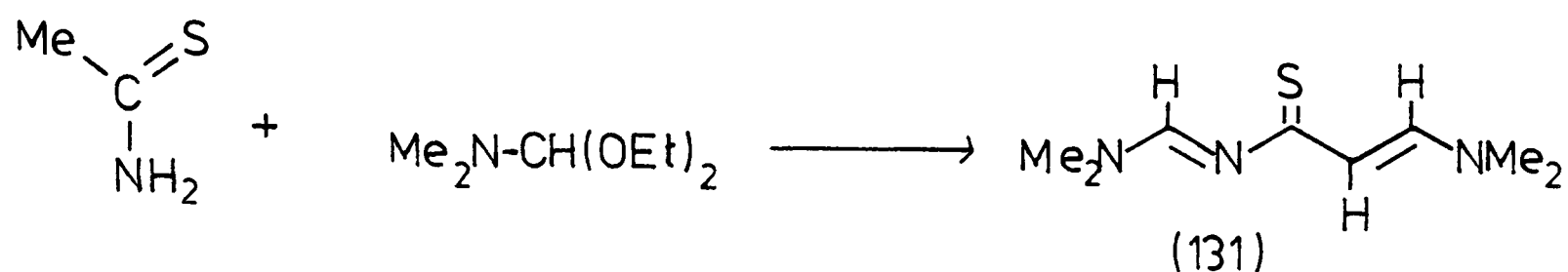
However, attempts to prepare the parent compound (R=H) by the same method, using formamide,¹³⁶ resulted in the formation of dimethylformamide, ethanol and hydrogen cyanide as shown in Scheme 113.



Scheme 113

It appears that with a hydrogen atom next to the amide

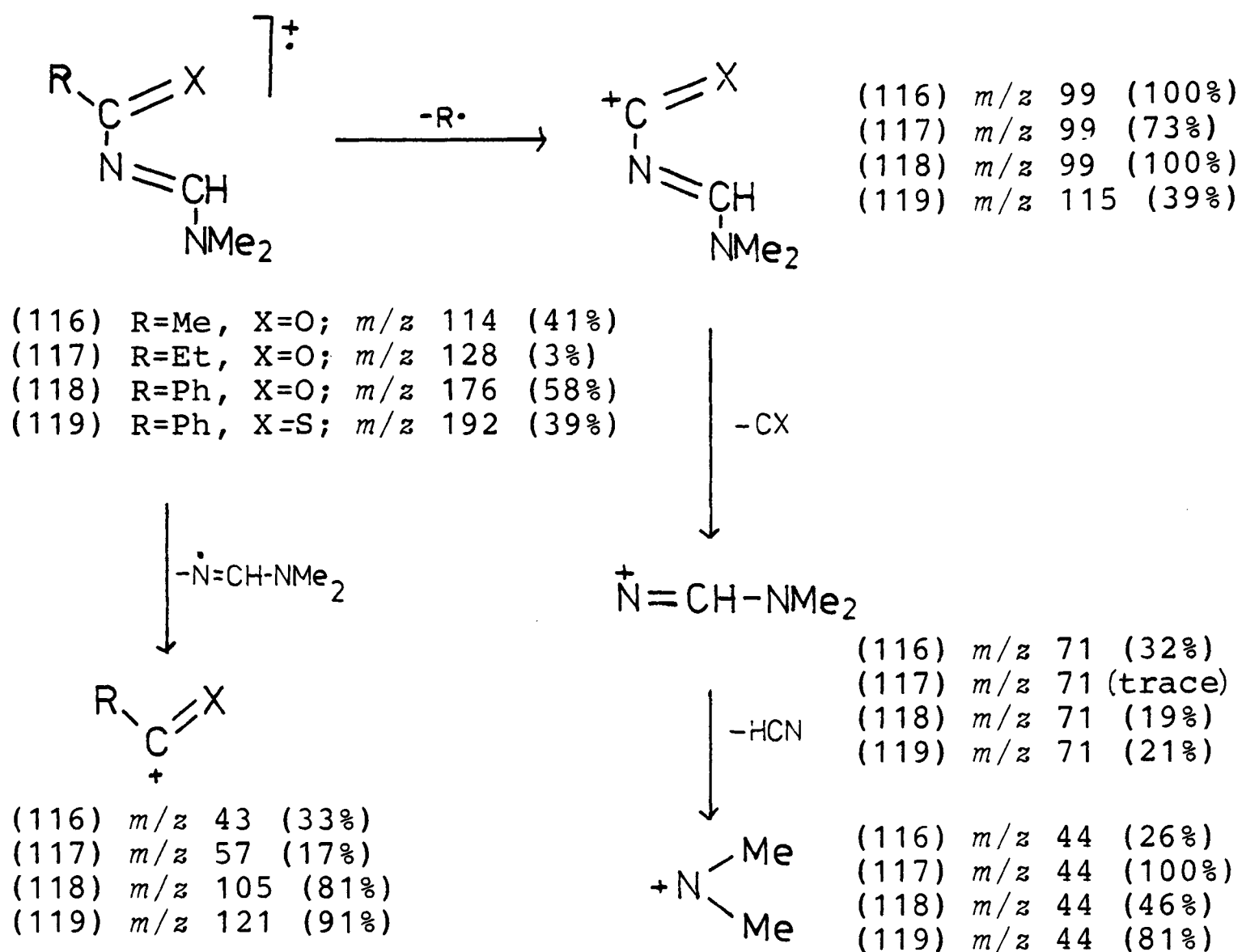
function, the oxygen is more readily alkylated than the central carbon of *N,N*-dimethylformamide diethylacetal. Similarly, attempts to prepare 3-dimethylamino-1-methyl-2-azaprop-2-en-1-thione were unsuccessful. The compound which did form was *N*-(3-aminothioacryloyl)-formamidine (131), due to the methyl of the thioamide being more activated by the thiocarbonyl than was the case with the carbonyl (Scheme 114).



Scheme 114

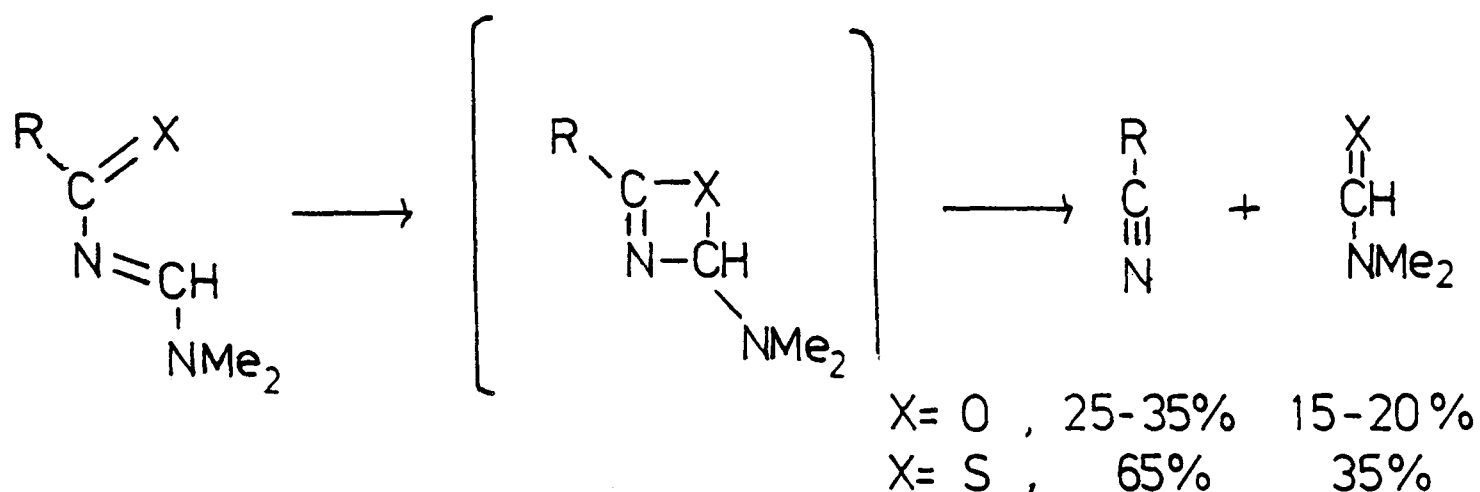
This reaction has since been reported by Liebscher.¹³⁷

The mass spectra of these 3-dimethylamino-2-azaprop-2-en-1-ones show that fragmentation under electron impact is very different to the thermal breakdown discussed later. There appear to be two possible pathways as shown in Scheme 115. The molecule either fragments with initial cleavage of the single C-N bond or else with loss of the alkyl radical followed by carbon monoxide (or CS) and then hydrogen cyanide.



Scheme 115

A furnace temperature of 900°C was required for complete reaction of all starting material under flash vacuum pyrolysis conditions, compared with the lower temperature of 650°C needed for the previous pyrolyses of azoalkenes (part B, sections II and III). In these examples an electron withdrawing oxygen or sulphur atom had been introduced into the general azoalkene structure (110) at position X and a methylene dimethylamino group replaced the *N*-phenyl group in the previous examples, at position Y. Despite these radical alterations, the mechanism of the reaction still appeared to be *via* the heteroazetidine intermediate, which fragmented to give *N,N*-dimethylformamide (or thioformamide) plus the appropriate nitrile, as shown in Scheme 116.

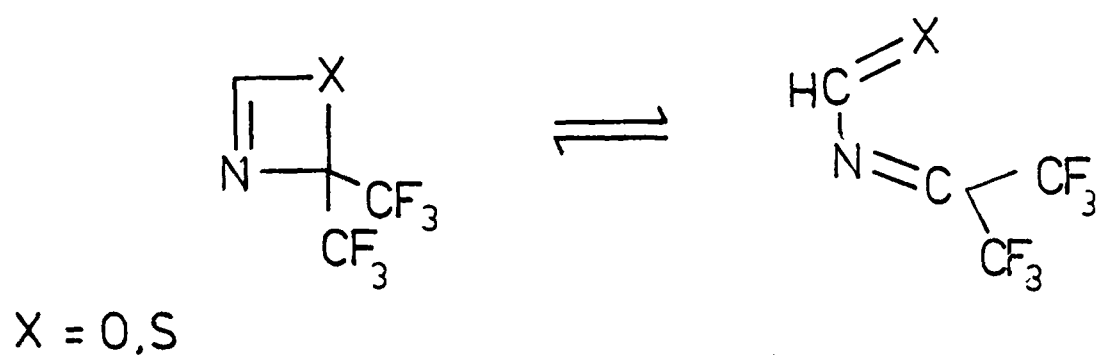
Scheme 116

Compared to the pyrolysis of the 1,4-diazabutadienes discussed in part B, section II, the pyrolysis product yields are very low. It was clear from g.c./m.s. and ^1H n.m.r. spectroscopy that these were the only clean thermal degradation products. The low yields could be caused by fragmentation reactions due to the high temperature conditions.

The significantly higher furnace temperature required here means that one of the steps in the reaction must have a higher activation energy than previous examples.

The major conformation of the compounds is transoid, therefore it is necessary for the molecule to twist into the cisoid formation before cyclisation can take place. Once the cyclisation has occurred there are two possibilities: cleavage of the intermediate to give the products found, or else ring opening back to the starting material.

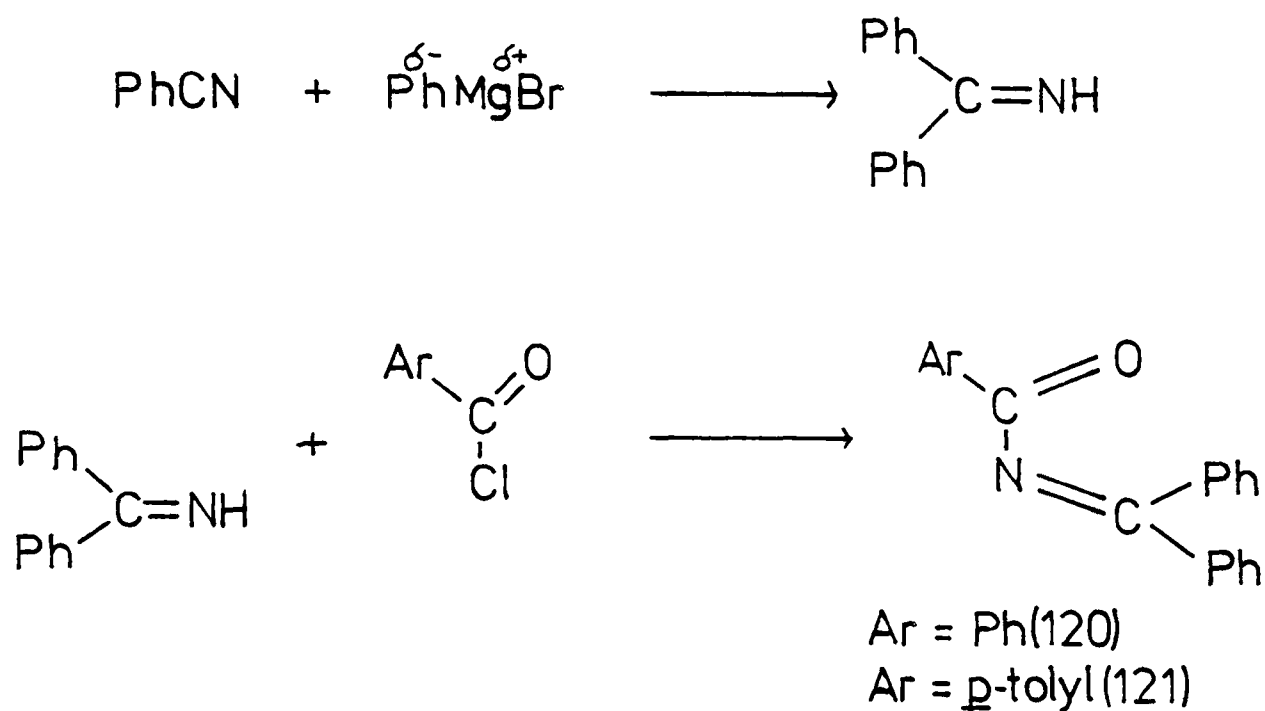
It has been reported that certain heteroazetines can be isolated and are in equilibria with the ring opened starting material¹³⁸⁻¹⁴⁰ (Scheme 117).

Scheme 117

Whereas the diazetines (cf. part B, section II) which are known as isolable compounds,¹⁴¹ appear to show less tendency to ring open, with the exception of one rather exotic example.¹⁴² This may therefore be a plausible explanation for the difference in furnace temperatures required for the different azadiene structures, as the energy profiles for the reactions of the various structures may be very different.

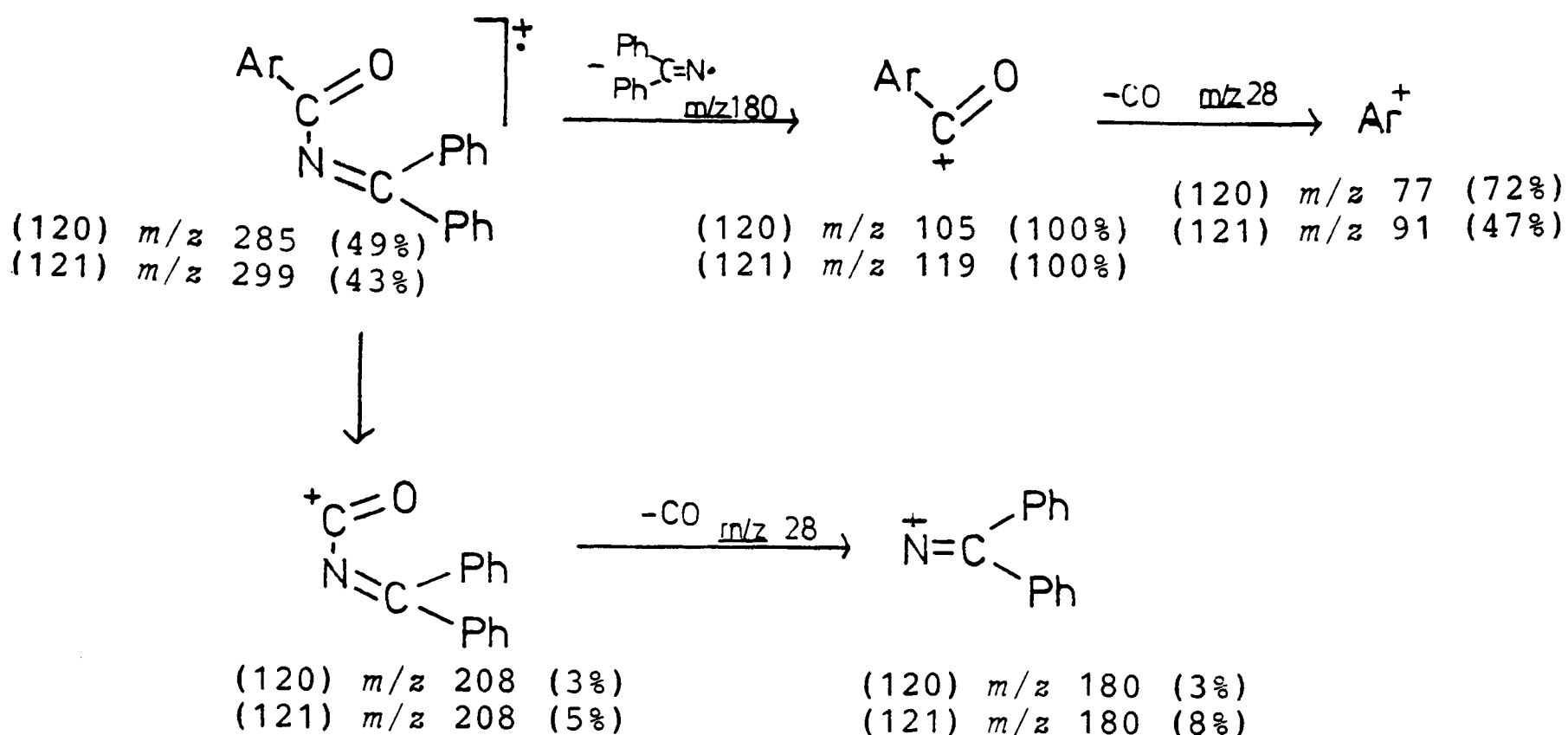
V Preparation, Properties and Pyrolysis of 1-Aryl-3,3-diphenyl-2-azaprop-2-en-1-ones

1-Aryl-3,3-diphenyl-2-azaprop-2-en-1-ones were obtained from the reaction of the appropriate aroyl chloride with benzophenone imine, which was prepared by reaction of a Grignard reagent with benzonitrile as shown in Scheme 118.



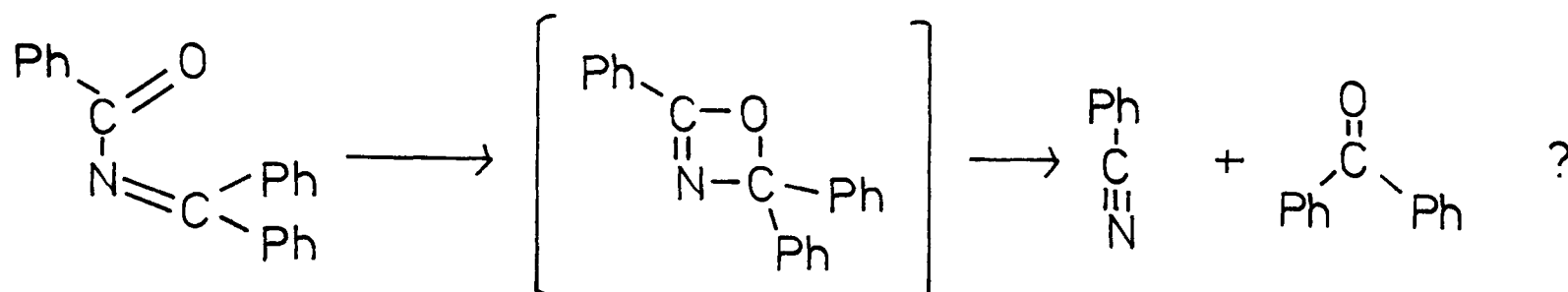
Scheme 118

The mass spectra of compounds (120) and (121) show that fragmentation under electron impact involves the cleavage of the C-N bond (Scheme 119).

Scheme 119

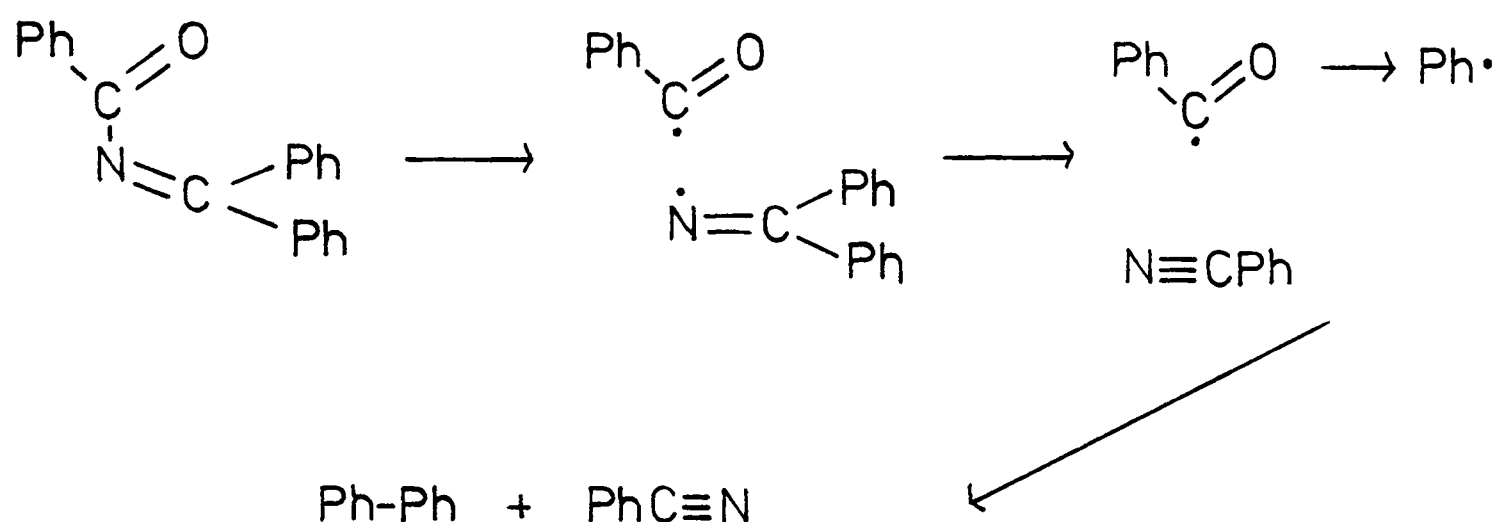
A furnace temperature of 900°C was required for complete reaction of the starting material on flash vacuum pyrolysis, as for the 3-dimethylamino-2-azaprop-2-en-1-ones (section IV).

If, as in the previous examples, pyrolysis of the starting material resulted in the formation of a diazetine intermediate which then fragmented, benzonitrile and benzophenone would be expected on pyrolysis of (120).

Scheme 120

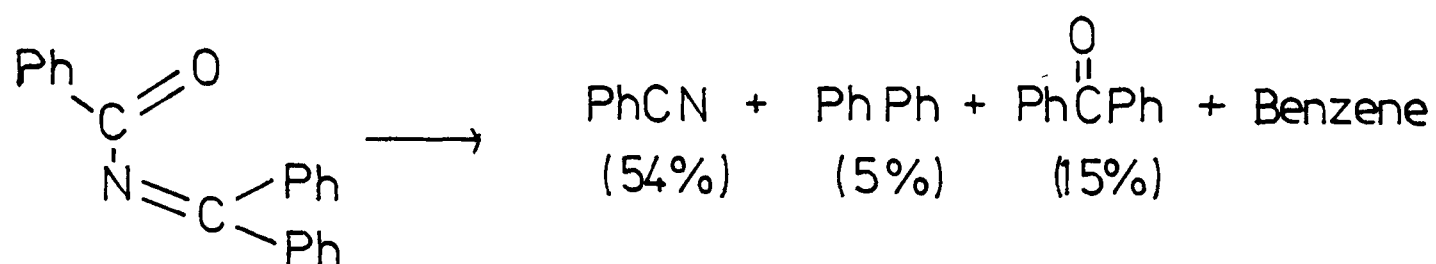
Both of these compounds were obtained but a considerable amount of biphenyl was also formed. This is explicable by cleavage of the single carbon nitrogen bond to form free radicals as

shown in Scheme 121. Benzoyl radicals would probably lose carbon monoxide to give an auxiliary source of phenyl radicals, as discussed in more detail in the next section; both benzil and benzophenone were found to be stable under the reaction conditions.



Scheme 121

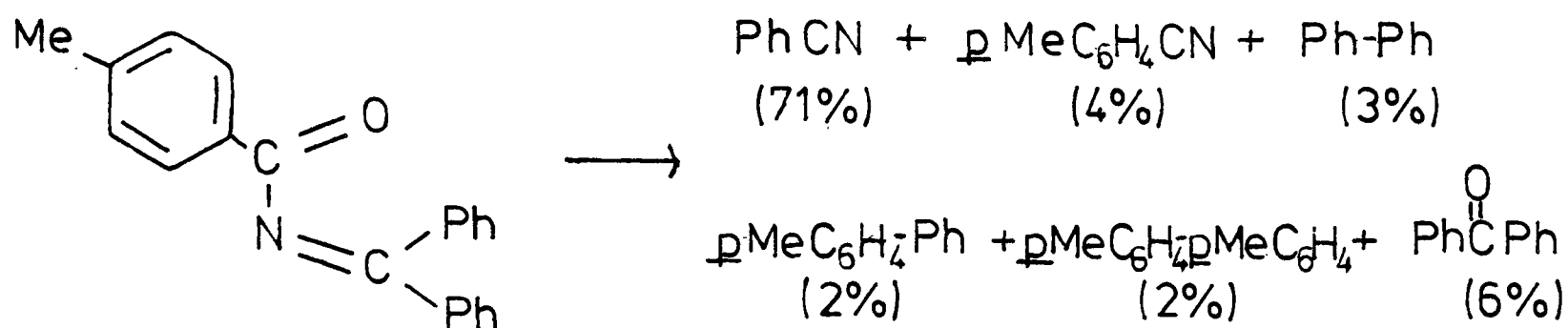
The presence of both biphenyl and benzophenone (Scheme 122) suggests there is the possibility of both reactions (Schemes 120 and 121) taking place.



Scheme 122

To discover how much, if any, of the starting 1,3,3-triphenyl-2-azaprop-2-en-1-one (120) was fragmenting *via* the four membered ring transition state and how much *via* the radical pathway, a methyl group was placed at the *para* position of the 1-phenyl ring. In this way the respective amounts of

p-methylbenzonitrile and benzonitrile could be compared. The *p*-methylbenzonitrile could only be formed from the cyclisation and not from the free radical breakdown. Gas liquid chromatography showed that the ratio of methylbenzonitrile:benzonitrile was 1:18 ie. less than 6% of the reaction followed the cyclisation pathway.



Scheme 123

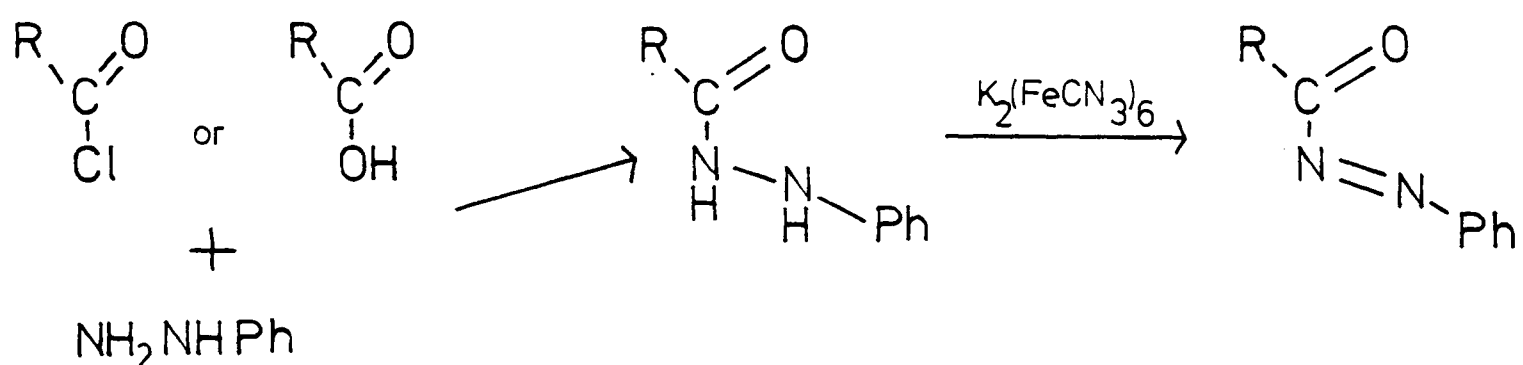
The complementary amounts of benzophenone expected for the cyclisation pathway were also found, although in both cases (Schemes 122 and 123) the yields of the benzophenone were higher than expected. This can be explained as compounds (120) and (121) are very prone to hydrolysis and may well have hydrolysed during manipulation or else on heating, in the inlet to the furnace.

The remaining 94% of the reaction followed the free radical pathway. The mixtures of biphenyls found from pyrolysis of (121) (Scheme 123) is good evidence for the random coupling of aryl groups, confirming a non-intramolecular mechanism. Data on the structure of compound (120) which has been reported by Allmann and Würthwein¹⁴³ is able to account for the predominance of the radical pathway in these examples.

They found that the interplanar angle $C=N-C=O$ was 73° showing that the molecule is twisted. A study of the bond lengths (using the valence bond method) showed that the central C-N bond has 80% single bond character and only 20% double bond character. This is in contrast with the heteroazadienes mentioned in earlier sections where the central C-N bond has considerably more double bond character as reflected in the restricted rotation discussed in Part C. Cleavage of the carbon nitrogen bond is therefore easier for compounds (120) and (121) compared with the heteroazadienes previously discussed. The interplanar angle and the bond lengths of (120) also indicate that there is little interaction between the $C=O$ and the $C=N$ groups. This is significant as it will increase the activation energy required for the first step of the cyclisation pathway.

VI Preparation, Properties and Pyrolysis of 3-Phenyl-2,3-diazaprop-2-en-1-ones

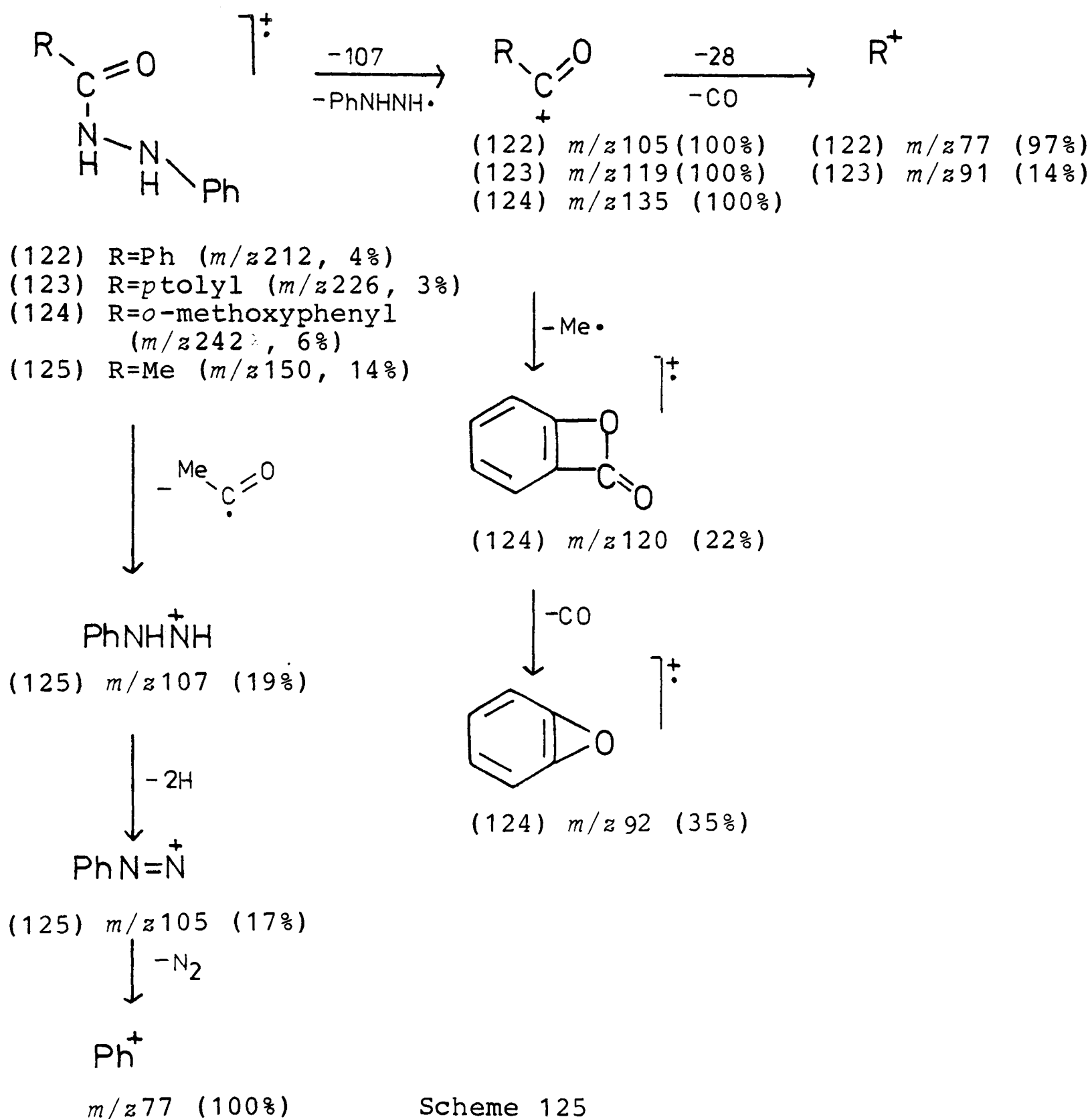
3-Phenyl-2,3-diazaprop-2-en-1-ones were obtained from the oxidation of the appropriate phenylhydrazides (which were colourless solids, prepared by the reaction of various acid chlorides with phenylhydrazine). The oxidation of the phenylhydrazides with potassium ferricyanide is reported in the literature using a two phase system and 2,4,6-tri(4-*t*-butylphenyl) phenol as a phase transfer catalyst. This phenol is not readily obtainable and therefore 2,4,6-tri-(*t*-butyl) phenol was used in its place. Great difficulty was experienced in trying to separate this phenol catalyst from the desired product with neither distillation or extraction of the phenol into base actually separating the two compounds. Eventually the reaction was attempted in the absence of the phenol and was found to proceed smoothly and with good yield of the desired product as a red oil, yet without a phase transfer catalyst present.



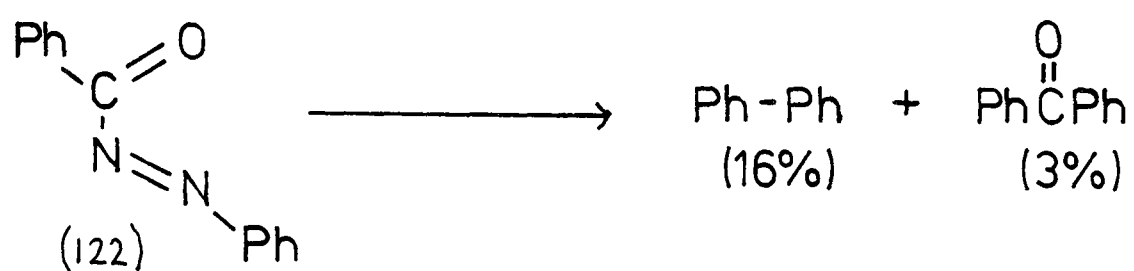
Scheme 124

<u>Compound No.</u>	<u>R</u>	<u>Compound No.</u>	<u>R</u>
(125)	Me	(123)	
(122)	Ph	(124)	

Compounds (125), (122), (123) and (124) all showed a peak at $(M+2)^+$ in the mass spectra. This may be due to the ease with which these compounds are reduced back to phenylhydrazide in the mass spectrometer. The main breakdown pattern under electron impact involves cleavage of the C-N bond (Scheme 125) as in previous examples and is closely related to the thermal fragmentation pattern to be discussed shortly.



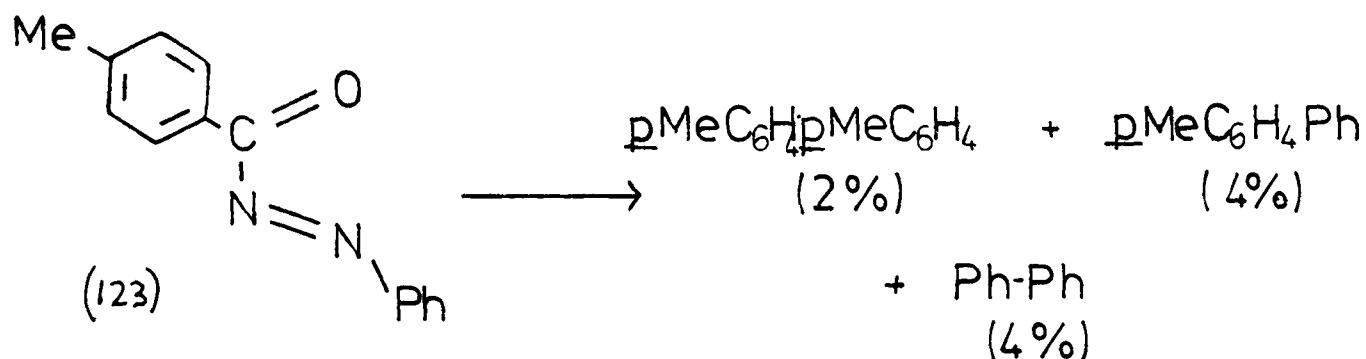
The flash vacuum pyrolysis of the 3-phenyldiazaprop-2-en-1-one was complete at a furnace temperature of 750°C. 1,3-Diphenyl-2,3-diazaprop-2-en-1-one (122) gave no benzonitrile but yielded biphenyl (16%), which is indicative of a radical mechanism taking place (Scheme 126).



Scheme 126

When pyrolysed on a large scale, benzene was also collected, presumably obtained from the phenyl radicals by high energy hydrogen abstraction processes. This may explain the low yields of radical coupling products. In general, phenyl radicals do not couple efficiently and yields of biphenyl of only 6-12% are obtained from precursors which are normally good radical generators.¹⁴⁴

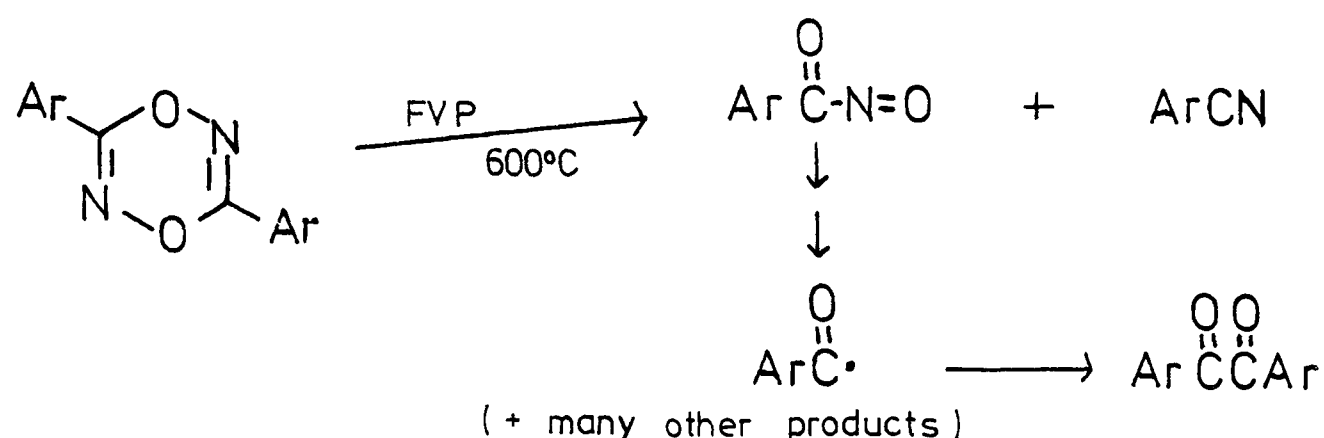
When a *p*-methyl group was placed on the phenyl ring, as in compound (123), various biphenyls were obtained as shown in Scheme 127, from coupling of the *p*-tolyl radicals as before.



Scheme 127

No benzophenone or benzil was found, which supports a radical mechanism with a very short lived aroyl radical. It is strange that the aroyl radical is unable to be trapped as a

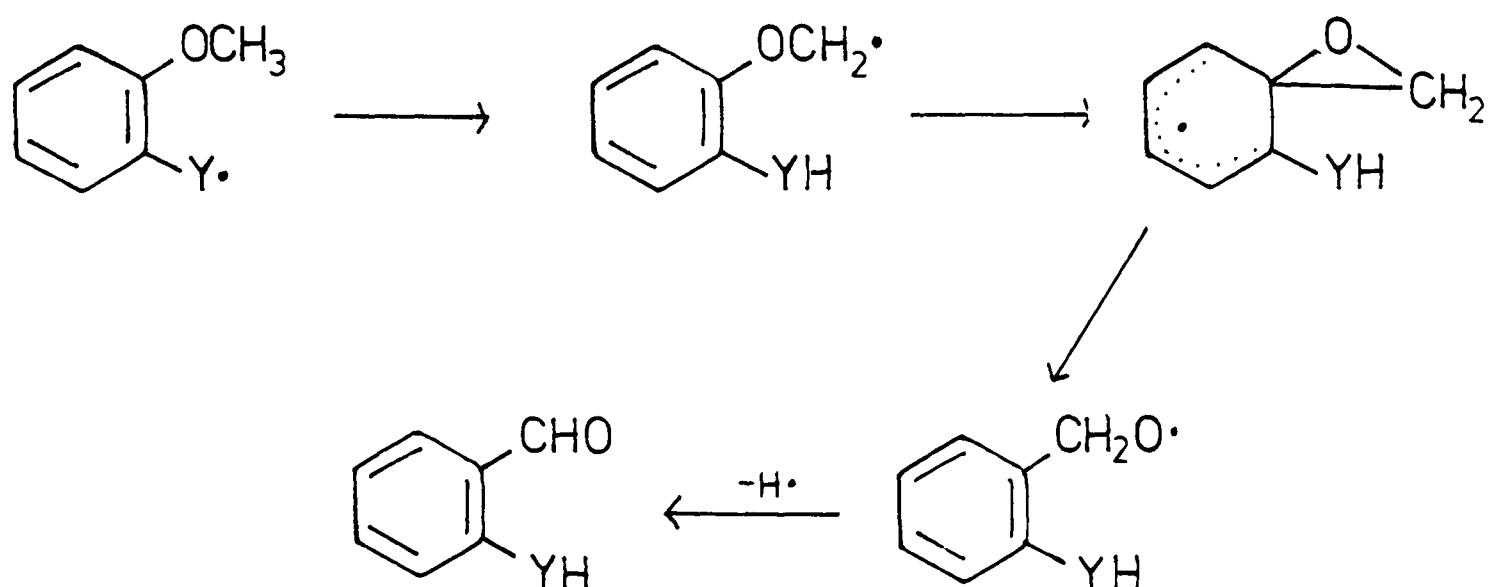
recent report¹⁴⁵ indicates that such radicals can couple under milder conditions, as shown in Scheme 128. The more severe conditions (ie. 900°C or 750°C) used here probably result in fragmentation by loss of carbon monoxide.



Scheme 128

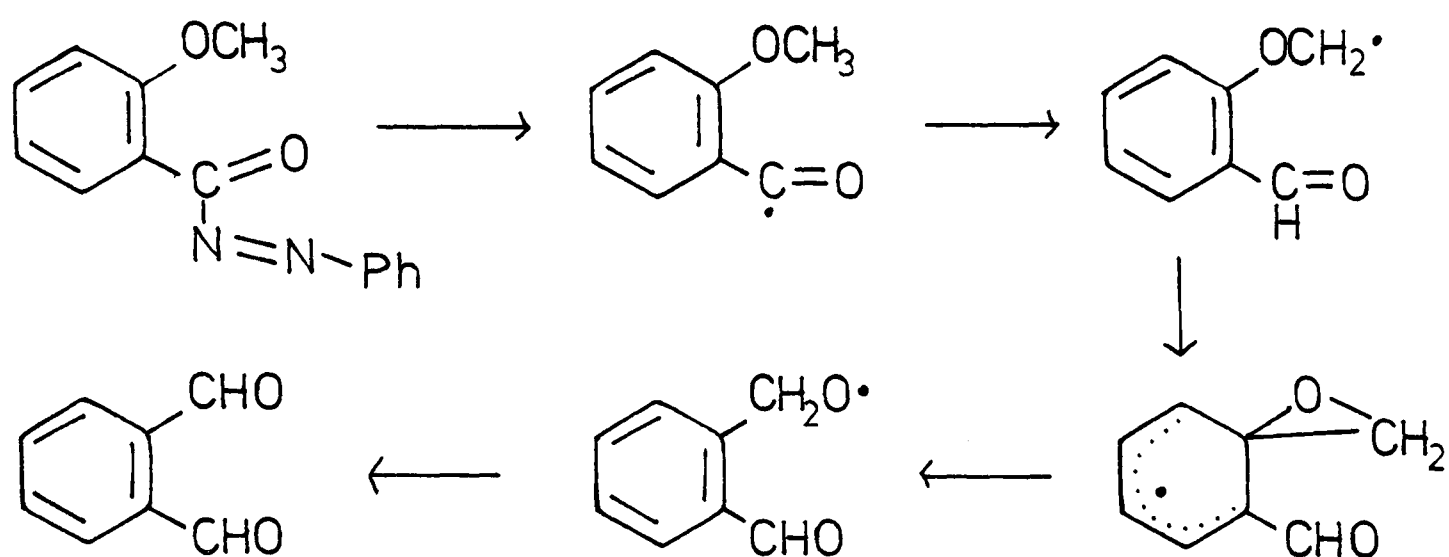
With the fragmentation of the aroyl radical firmly established it was of interest to see if an intramolecular reaction which might proceed faster than gas phase fragmentation followed by coupling, could be used to trap the aroyl radical.

De Mayo¹⁴⁷ has reported the use of an *o*-methoxy group for the intramolecular trapping of radicals as shown in Scheme 129. This has recently been shown to be general for a range of Y and *ortho* groups.^{148, 20}



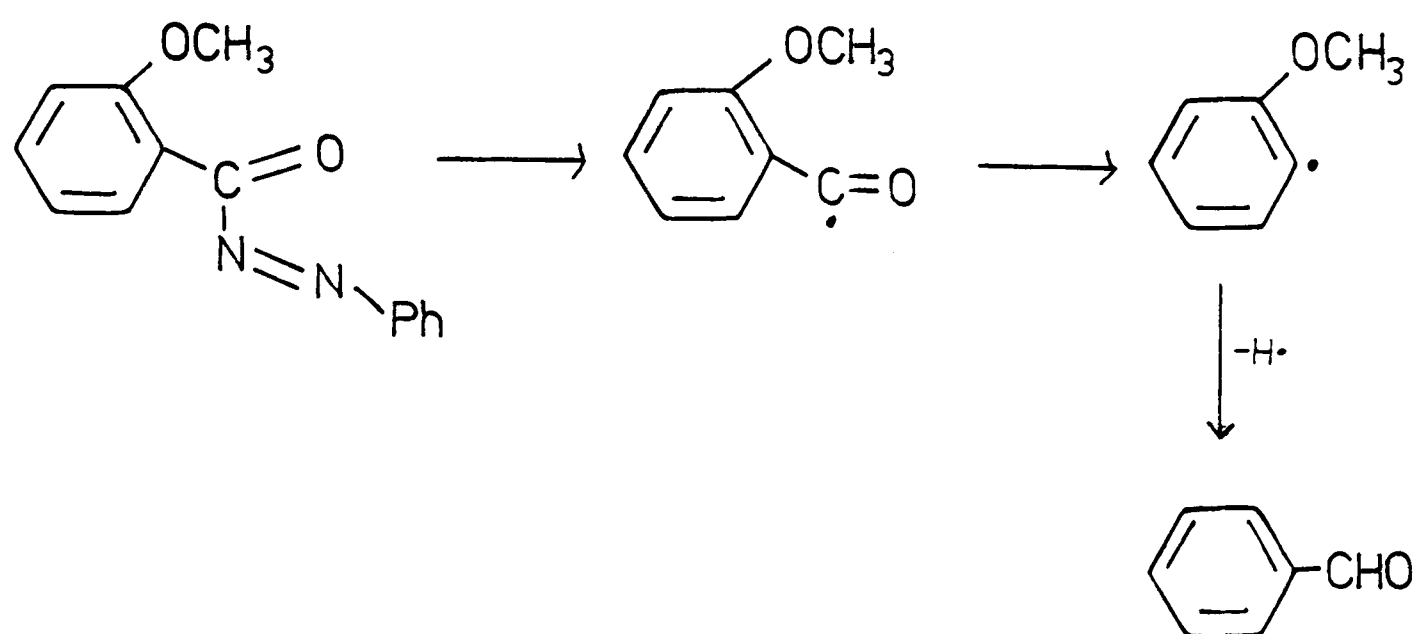
Scheme 129

The pyrolysis of 1-*o*-methoxyphenyl-3-phenyl-2,3-diazaprop-2-en-1-one (124) was therefore of particular interest, as, if the aroyl radical could be intramolecularly trapped, as shown in Scheme 130, the resulting product would be phthalaldehyde. Substituted phthalaldehydes are fairly difficult to prepare but synthetically very useful, particularly in the preparation of quinazolines.



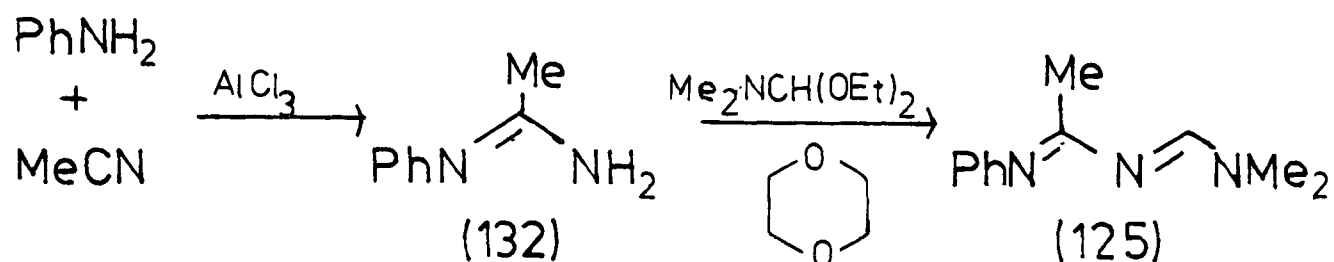
Scheme 130

The pyrolysate of (124) was carefully examined and the ^1H n.m.r. spectrum showed that an aldehyde was present. However comparison of the pyrolysate with an authentic sample of phthalaldehyde using the gas chromatogram showed that phthalaldehyde was not in fact present in the pyrolysate. The aldehyde present was found to be benzaldehyde. This shows that the aroyl radical must be losing carbon monoxide prior to hydrogen transfer, to leave the *o*-methoxyphenyl radical which then rearranges with loss of a hydrogen atom to give benzaldehyde as shown in Scheme 131.

Scheme 131

VII Preparation, Properties and Pyrolysis of 5-Phenyl-1,1,4-trimethyl-1,3,5-triazapentadiene

5-Phenyl-1,1,4-trimethyl-1,3,5-triazapentadiene (125) was prepared as shown in Scheme 132.

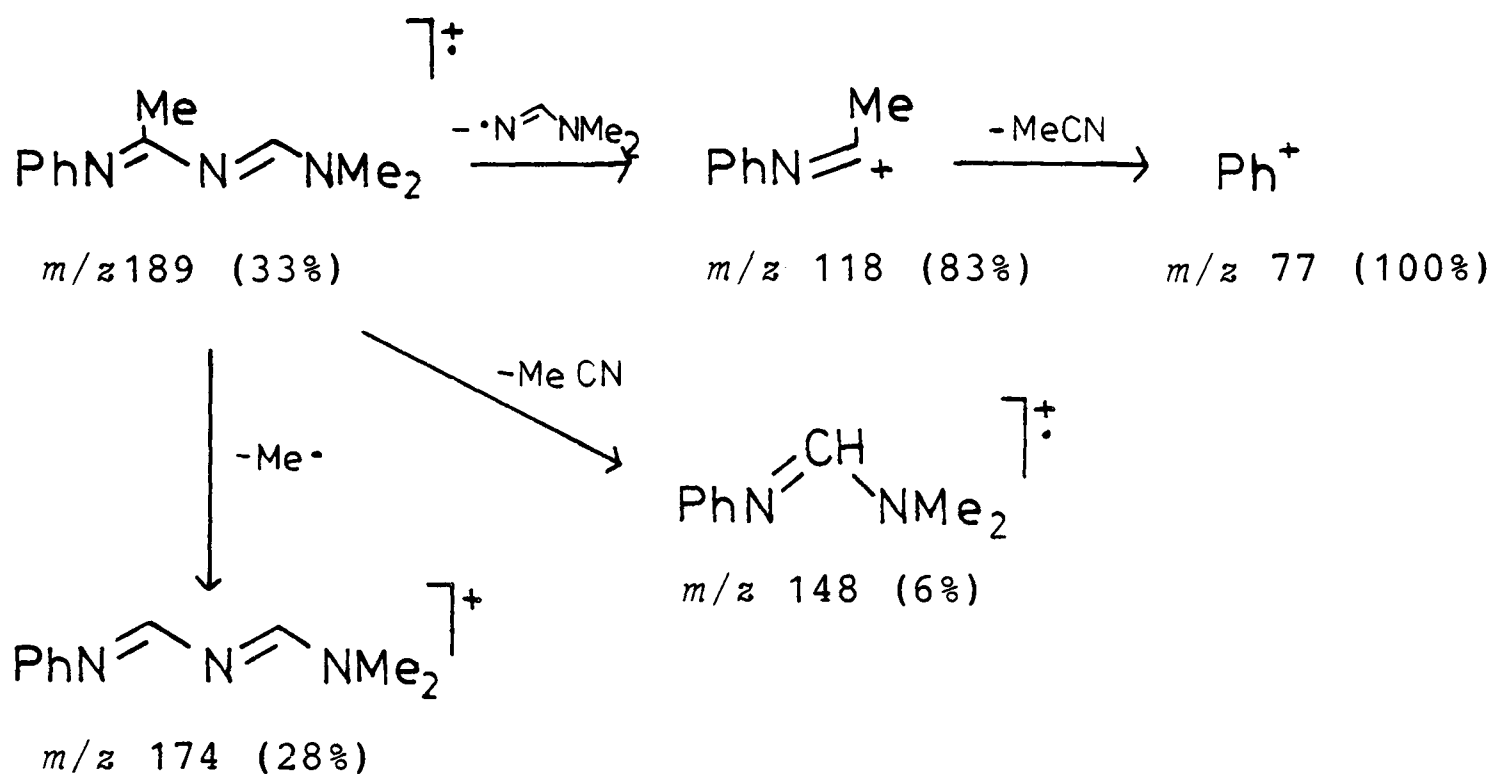


Scheme 132

N-Phenylacetamidine (132) was prepared from aniline and acetonitrile, using aluminium chloride as a catalyst. It was immediately converted into the picrate as this helped with both purification and storage. To prepare the desired triazapentadiene (125), the amidine (132) was reconverted from the picrate and reacted with *N,N*-dimethylformamide diethyl-acetal.

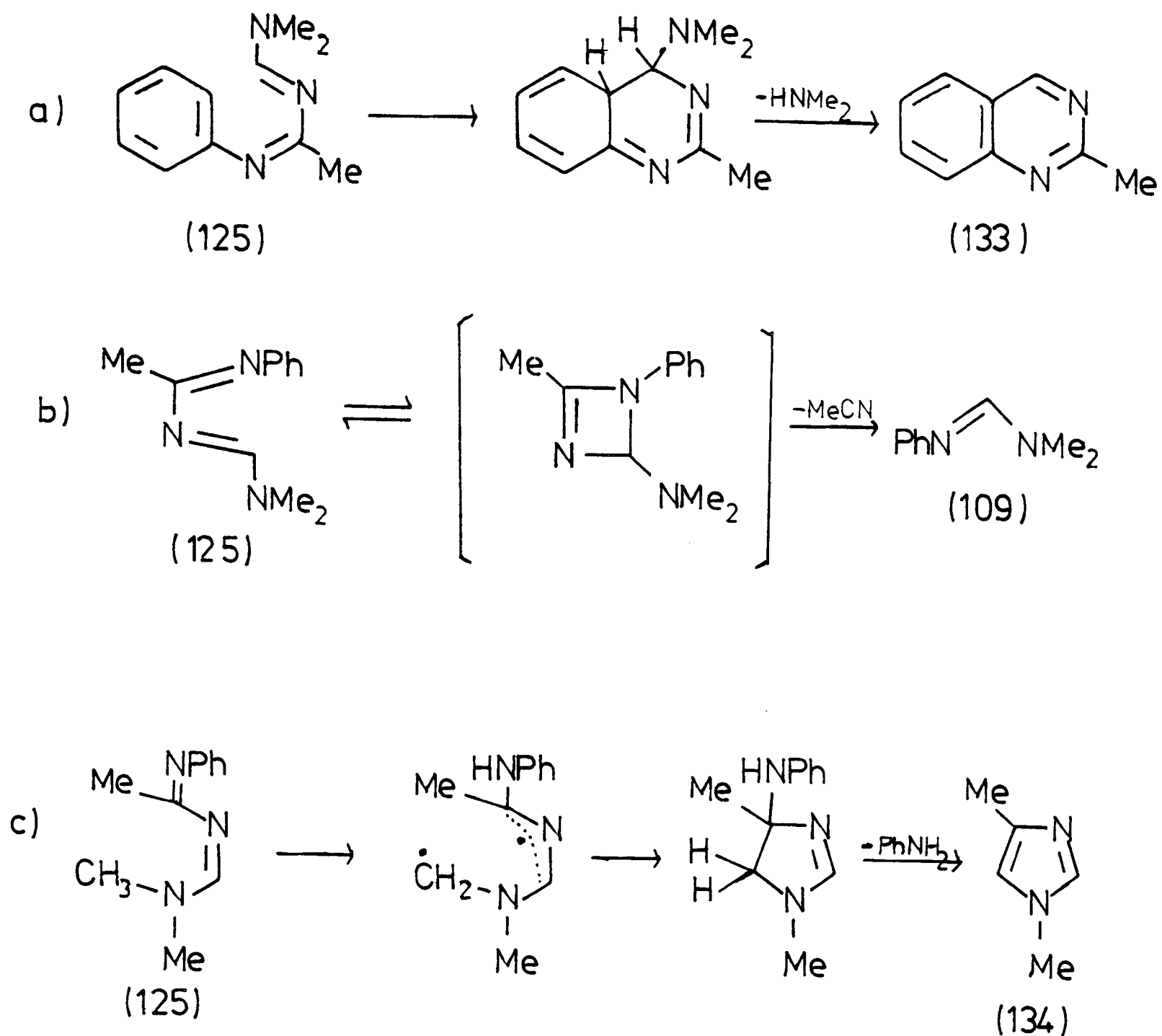
It had been hoped to prepare 1,1-dimethyl-5-phenyl-1,3,5-triazapentadiene using *N*-phenylformamidine and *bis*-dimethyl-amino-*t*-butyloxymethane (which is more reactive than the diacetal) but the desired product was not obtained.

The mass spectra of (125) indicated that the main fragmentation under electron impact involved cleavage of the C-N bond as shown in Scheme 133.

Scheme 133

There was no evidence for cyclisation *via* an intramolecular hydrogen transfer¹¹² (no peak at m/z 84 or 69) or for a 6π cyclisation with elimination (no peak at m/z 144). It was possible that some of (125) had fragmented *via* an azetine intermediate as there was an appropriate peak [m/z 148 (6%)] which could indicate the presence of 3,3-dimethyl-1-phenyl-1,3-diazapropene although no metastable peak was present to confirm this.

There are several possible thermolytic pathways for compound (125). It is analogous to the compounds used by Jutz in 6π cyclisation with elimination reactions (discussed in the introduction part B, section II(b)) and may therefore undergo the reaction shown in route (a) of Scheme 134. It could also undergo a reaction similar to compounds (109-114) and (116-119), passing through an azetine intermediate before breaking down to give acetonitrile and 3,3-dimethyl-1-phenyl-1,3-diazapropene (109) (route (b), Scheme 134).



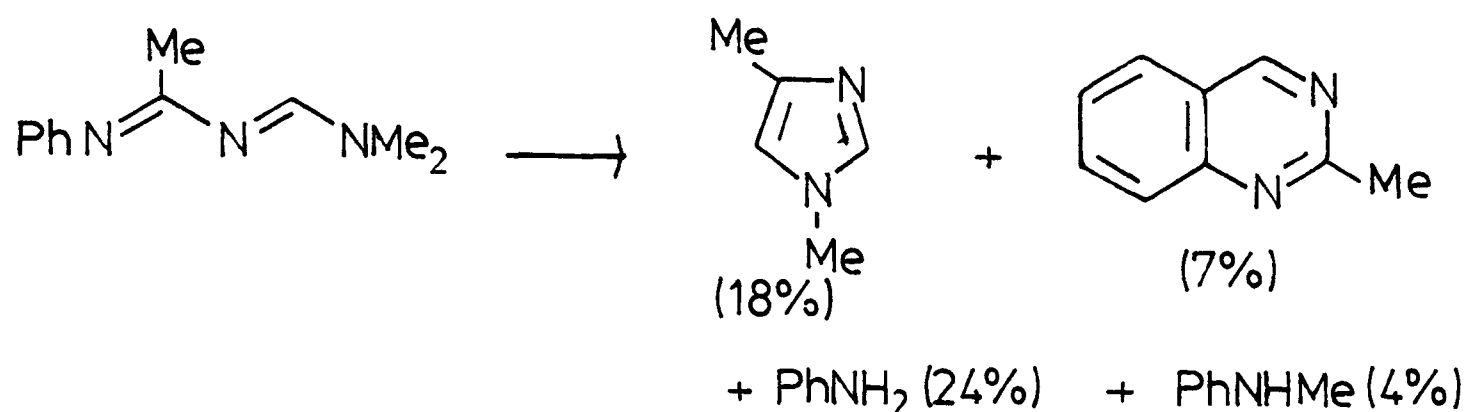
Scheme 134

Compound (125) is also analogous to the 1,5-diazapentadiene discussed in part A. Therefore, an intramolecular hydrogen transfer followed by ring closure and elimination is a plausible pathway (route (c), Scheme 134) leading to the formation of 1,4-dimethylimidazole.

The flash vacuum pyrolysis of (125) required a furnace temperature of 800°C. The pyrolysate was carefully examined for the presence of 3,3-dimethyl-1-phenyl-1,3-diazapropene (109), 2-methylquinazoline (133) and 1,4-dimethylimidazole

(134), as all three appeared to be possible products of the pyrolysis.

The pyrolysate was found to contain 1,4-dimethylimidazole (18%) and 2-methylquinazoline (7%), along with aniline (24%) and *N*-methylaniline (4%) (Scheme 135).



Scheme 135

It is the most unusual of the three possible routes (route (c), Scheme 134) which apparently has the lowest activation energy and therefore is the most favourable pathway. The 6π electrocycloisatation (route (a)) is a competing process, yet it competes to a lesser extent than one might expect, compared with the 1,5-diazapentadiene analogue (91). The extra nitrogen in the middle of the pentadiene chain appears to favour the hydrogen transfer relative to the electrocycloisatation. It is most surprising that no 3,3-dimethyl-1-phenyl-1,3-diazapropene was found in the pyrolysate, especially when compared with the pyrolysate of the analogous compound (116). Replacement of the oxygen atom of (116) by an *N*-phenyl group appears to make intramolecular hydrogen transfer more favourable. It has now been found¹⁴⁹ that hydrogen transfer is generally the favourable reaction, when the hydrogen is transferred to the nitrogen atom of an imine group rather than the oxygen or sulphur atom of a

VIII CONCLUSION

Having made and pyrolysed an extensive selection of azadienes, it appears that the 4π electrocyclisation followed by cleavage and elimination of nitrile, is general over a wide range of azadienes. However this reaction can take an alternative course whenever the central bond becomes weak due to poor conjugative interaction between the two double bonds of the heterodiene. When this is possible, the thermolysis reactions are dominated by radical cleavage of the central bond. Another minor exception is when there is a dimethylamino group able to transfer a hydrogen to a remote *N*-phenyl group, leading to five membered ring products, as is the case with compound (125).

C. Variable Temperature Proton N.M.R. Spectroscopy Studies

Many of the dimethylamino compounds discussed in sections 1 and 2 are of particular interest for study by variable temperature ^1H n.m.r. spectroscopy. This is due to the delocalisation of electrons throughout the extended amide and the restricted rotation of the dimethylamino group.

Two classes of compounds can be identified from the previous sections, the 1,5-diazapentadienes and their 1,3,5-triazapentadiene analogues. In addition, the 1,2,5-triazapentadiene analogues are readily available.¹⁵⁰ This will enable the effect of a nitrogen atom at various positions of the pentadiene chain to be studied. The corresponding salts were also known and would be expected to dramatically effect the electron delocalisation. This effect could be studied more systematically by using the quaternary salt and also the carbonyl analogue. Finally, it was possible to make estimates of the effect of a methyl group at various sites of the conjugated system by studying compounds which had been prepared for different investigations in previous sections.

The range of compounds which was studied is shown in Table 6. The preparation of most of these compounds was discussed in earlier sections. Some compounds were available from previous work in Edinburgh.¹⁵¹ The gaps in the table were filled as much as possible by preparing the appropriate compounds specially for variable temperature n.m.r.

For example, compounds (136), (137) and (138) were prepared as shown in Scheme 136.

COMPOUNDS OF INTEREST FOR STUDY BY VARIABLE TEMPERATURES

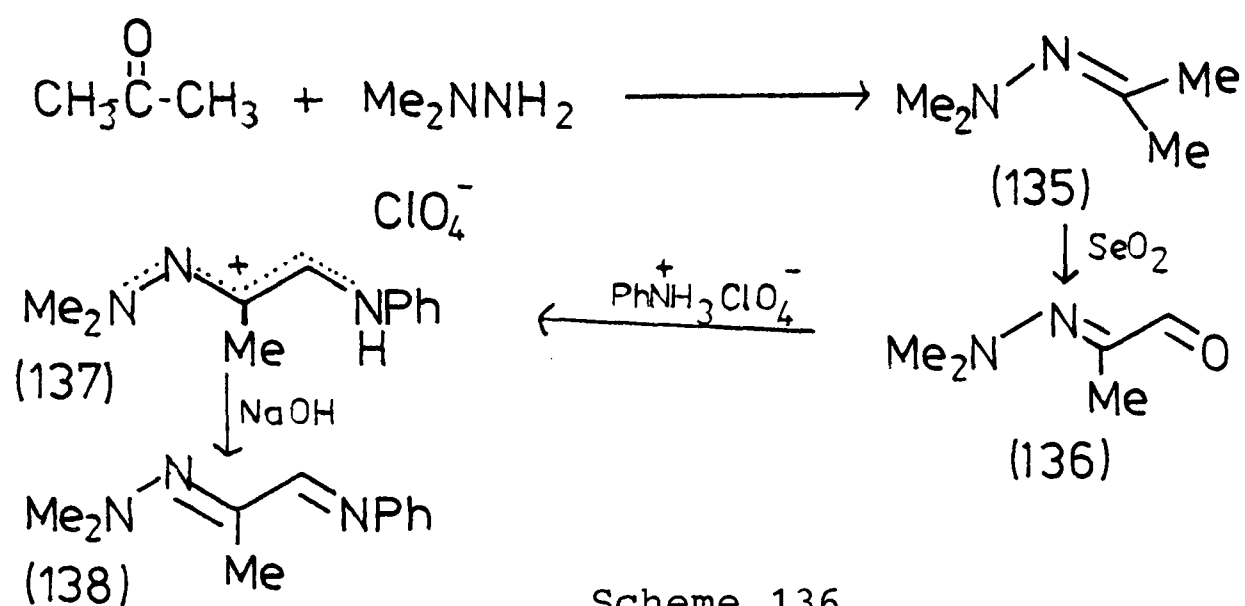
¹H N.M.R. SPECTROSCOPY

	X=	O	NPh	(⁺) NPh H	(⁺) NMe ₂	S
	(i)	(145) ^a	(146) ^a	(147) ^a	(148) ^a	-
	(ii)	(136) ^d	(138) ^d	(137) ^d	- ^e	-
	(iii)	(149) ^a	(150) ^a	(151) ^a	- ^e	-
	(iv)	(140) ^d	(76) ^b	(75) ^b	(139) ^d	-
	(v)	(93) ^b	(95) ^b	(94) ^b	(92) ^b	-
	(vi)	(141) ^d	(85) ^b	(84) ^b	(144) ^d	-
	(vii)	(94) ^b	(91) ^b	(90) ^b	(92) ^b	-
	(viii)	(152) ^a	- ^e	- ^e	(153) ^a	-
	(ix)	(116) ^c	(125) ^c	(154) ^c	- ^e	-
	(x)	(118) ^c	-	-	-	(119) ^c

Table 6

Footnotes to Table 6

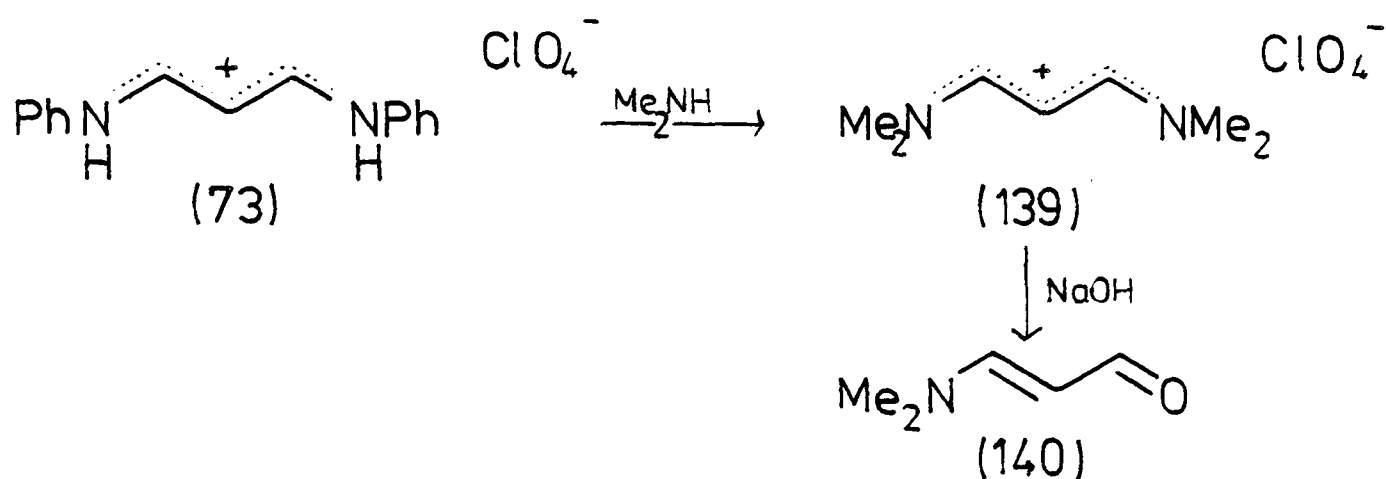
- a = compound available, usually obtained from H. McNab;
 b = compound prepared for f.v.p. study; preparation discussed in section 1;
 c = compound prepared for f.v.p. study; preparation discussed in section 2;
 d = compound prepared specially for study by variable temperature proton n.m.r. spectroscopy;
 e = compound not prepared i.e. gap in series.

Scheme 136

Acetone dimethylhydrazone (135) was formed from the reaction of acetone and *N,N*-dimethylhydrazine. This was then oxidised using selenium dioxide to give pyruvaldehyde-2-dimethylhydrazone (136) which, when treated with anilinium perchlorate yielded 5-phenyl-1,1,3-trimethyl-1*H*-1,2,5-triazapentadienium perchlorate (137). This was readily converted to the corresponding triazapentadiene (138) on treatment with sodium hydroxide. The quaternary salt was unable to be prepared by reaction of the hydrazone (136) with dimethylammonium perchlorate.

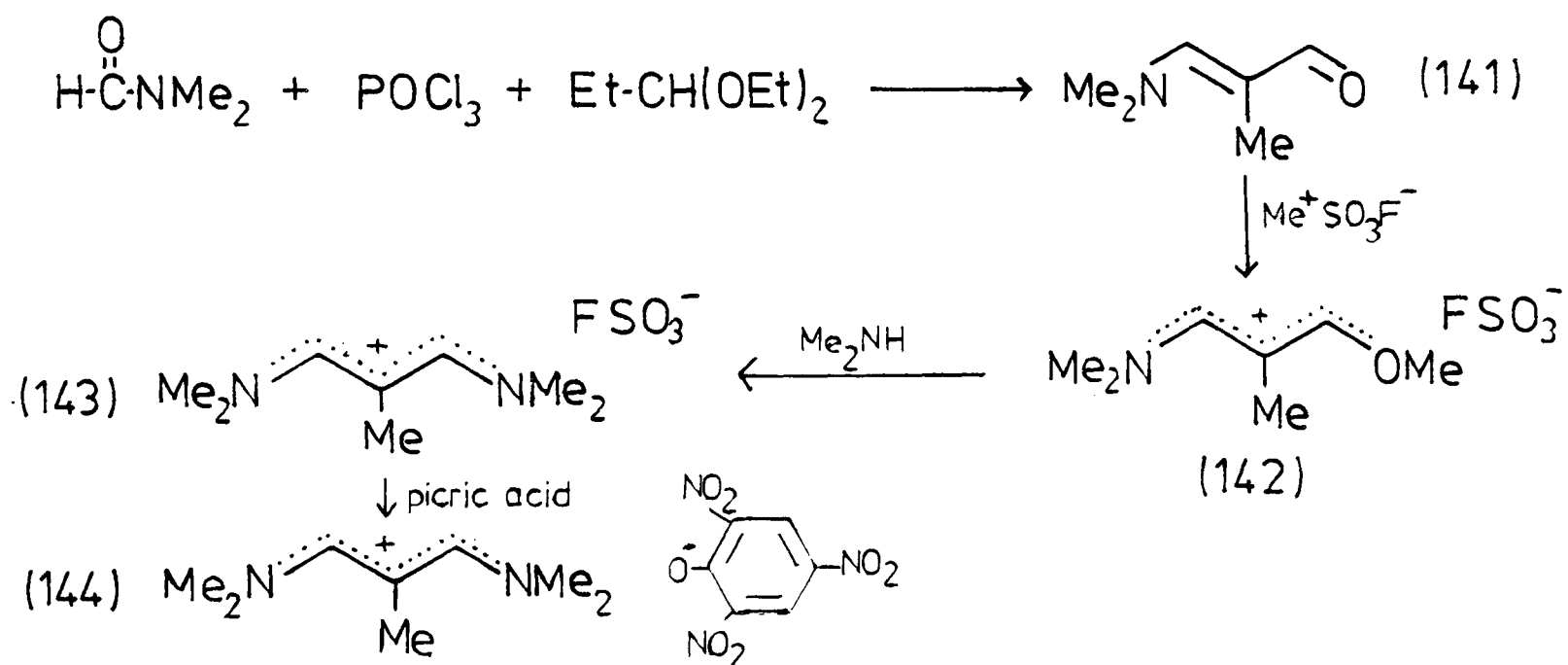
A similar route was used to prepare 1,1,5,5-tetramethyl-1*H*-1,5-diazapentadienium perchlorate (139) as was used for the

pentamethyl analogue (92) (Scheme 85). 1,5-Diphenyl-1*H*-1,5-diazapentadienium perchlorate (73) was treated with an excess of dimethylamine to give the desired product (139). When (139) was then hydrolysed with sodium hydroxide, dimethylaminoacrolein (140) was obtained (Scheme 137).



Scheme 137

Attempts to prepare 1,1,3,5,5-pentamethyl-1,2,5-triazapentadienium perchlorate by a similar method proved unsuccessful. However, it was possible to prepare the fluorosulphonate salt as shown in Scheme 138 (cf. Scheme 81).



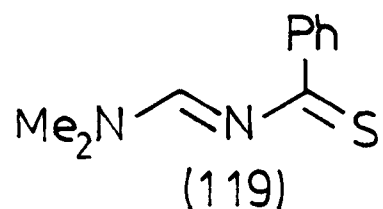
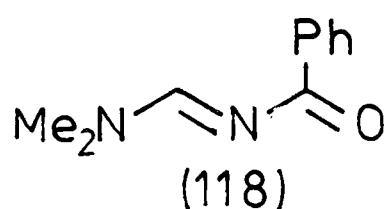
Scheme 138

After treating dimethylformamide with phosphonyl chloride, the resulting product was reacted with propionaldehyde diethylacetal to obtain 3-dimethylamino-2-methylacrolein (141). The acrolein (141) was then treated with methylfluorosulphonate to

give (142) which, when treated with an excess of dimethylamine, gave the desired product (143) as a fluorosulphonate salt. This was converted into the picrate salt (144) by treatment with picric acid.

There were however spaces in some of the series which remained unfilled due to several attempts to prepare a compound proving unsuccessful. For example, 5-phenyl-1,1-dimethyl-1,3,5-triazapentadiene could not be prepared by the same method as its trimethyl analogue (125). 1,1,4,5,5-Pentamethyl-1,2,5-triazapentadienium perchlorate was also unavailable due to the unreactivity of the ketone carbonyl, and 1,1,4,5,5-pentamethyl-1,3,5-triazapentadienium perchlorate was not obtained as the route through to (125) was inapplicable for making a salt.

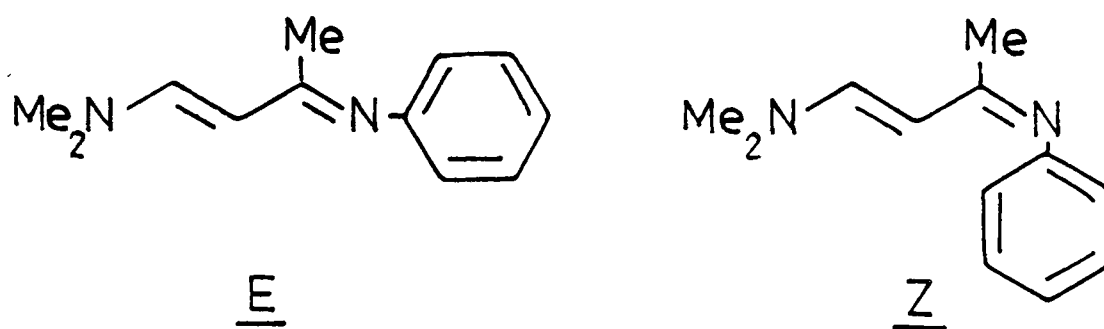
To observe the effect of a thiocarbonyl group as part of



the pentadiene chain, (118) and (119) were compared as it was not possible to make the methyl substituted analogue of (119) as discussed on page 99.

Room temperature n.m.r. spectra of the conjugated systems were unexceptional.^{150,152} However, there were two exceptions, where there was evidence of isomerisation in the conjugated system.

Firstly, the ¹H n.m.r. spectra of compounds with a methyl group on the carbon adjacent to the *N*-phenyl group showed two isomers to be present. This is due to the position of the phenyl ring being fixed in an *E* or *Z* configuration. This has



been previously reported for related systems^{68,153} and has now been supported in one case by ^{13}C n.m.r. spectroscopy (Table 7). When there is a methyl group adjacent to the

^{13}C N.M.R. Spectra of Trimethyl-1,5-diazapentadienes

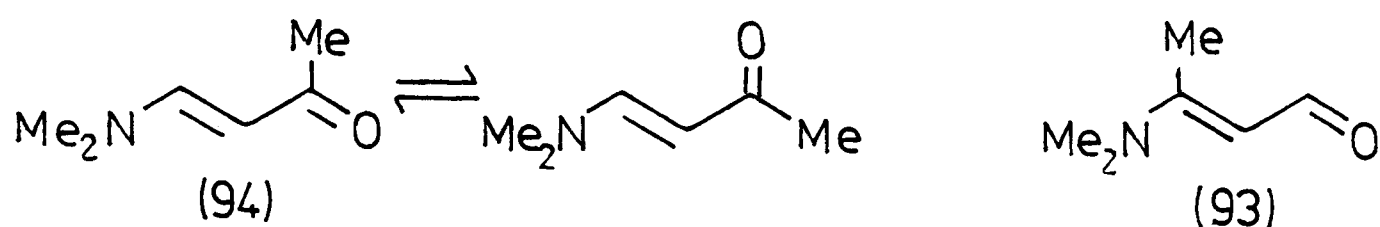
	C(2)	C(3)	C(4)
	164.26/165.09 (q)	92.33/100.06	148.07/146.74
	165.28	105.84(q)	152.26
	159.58	99.08	156.73(q)

Table 7

N-phenyl group, the large methyl group twists the phenyl group out of the plane and the signal for the methyl group is transmitted at a lower frequency. An equilibrium amount of the *Z* configuration is also adopted due to the bulky methyl group. However, an exception is observed for one compound with a methyl group on the carbon adjacent to the *N*-phenyl group. There was no clear evidence for the presence of two isomers for compound

(125) which has a nitrogen atom in the centre of the penta-diene chain. This is possibly due to the lack of the central hydrogen atom which may lead to a 100% *Z* configuration.

Another example of isomerisation in the conjugated system was observed for compound (94). This compound was obtained only as a mixture with compound (93).



The variable temperature ^1H n.m.r. was complicated at low temperatures by a further isomerisation. Since the olefinic coupling constants of both frozen isomers were identical, this isomerisation was identified as being due to restricted rotation about the single C-C bond. In addition, at normal temperatures only one peak was observed in the ^1H n.m.r. spectra for the C-methyl which indicated the average position of the methyl group. However at temperatures below -34.5°C (238.5K), two C-methyl peaks were present, indicating the presence of the two isomers, frozen in their respective configurations. From this behaviour the ΔG^\ddagger value for rotation around the single C-C bond was calculated as 50.6kJmol^{-1} .

Variable temperature ^1H n.m.r. spectroscopy of the compounds in Tables 6 and 9, is able to examine the rotation of the dimethylamino group about the terminal C-N (or N-N) bond. In general, at low temperatures two peaks are often observed due to an *E* methyl and a *Z* methyl group, effectively frozen in that configuration. However, at high temperatures only

one peak is often observed due to rapid rotation in the n.m.r. time scale about the N-C or N-N bond. At intermediate temperatures, a single broad peak can be observed and the coalescence temperature (T_c) is the temperature at which this peak has a flat top. From this coalescence temperature, the energetics of the process can be measured using the formula given below:

$$\Delta G^\ddagger = 19.13 T_c (9.97 + \log_{10} \frac{T_c}{\Delta\nu}) \text{ Jmol}^{-1}$$

where T_c = coalescence temperature

$\Delta\nu$ = maximum separation of frozen peaks in Hz.

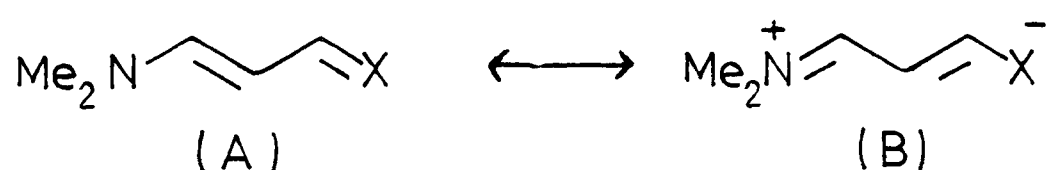
The compounds studied by variable temperature ^1H n.m.r. spectroscopy are shown in Tables 6, 9 and 11. Some isolated members of these series have been studied previously,^{150,152,154,155,156} but this is the first time a comprehensive range of compounds has been studied, with all measurements and readings recorded using the same instrument (Bruker WP 200) and with a restricted range of solvents. It is not possible for one solvent to be used throughout a temperature range from -100°C to $+200^\circ\text{C}$ therefore, considering the polarity of the salts to be studied, d_6 -acetone was used at low temperatures and d_6 -dimethylsulphoxide was used at high temperatures. It was assumed that there was little solvent effect, although this was checked on (140), where both solvents were used and measurements taken. From the results obtained (Table 8) it would have been possible to apply a correction factor, however, because the low measurements were so low and the high measurements were so high, this was not considered to be necessary due to the small correction factor.

Compound	Solvent	$\Delta\nu$ (Hz)	T_c (°K)	ΔG^\ddagger (KJmol ⁻¹)
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CHO}$ (140)	d_6 -acetone	63.66	314	64.0
	d_6 -d.m.s.o.	59.24	334	68.5

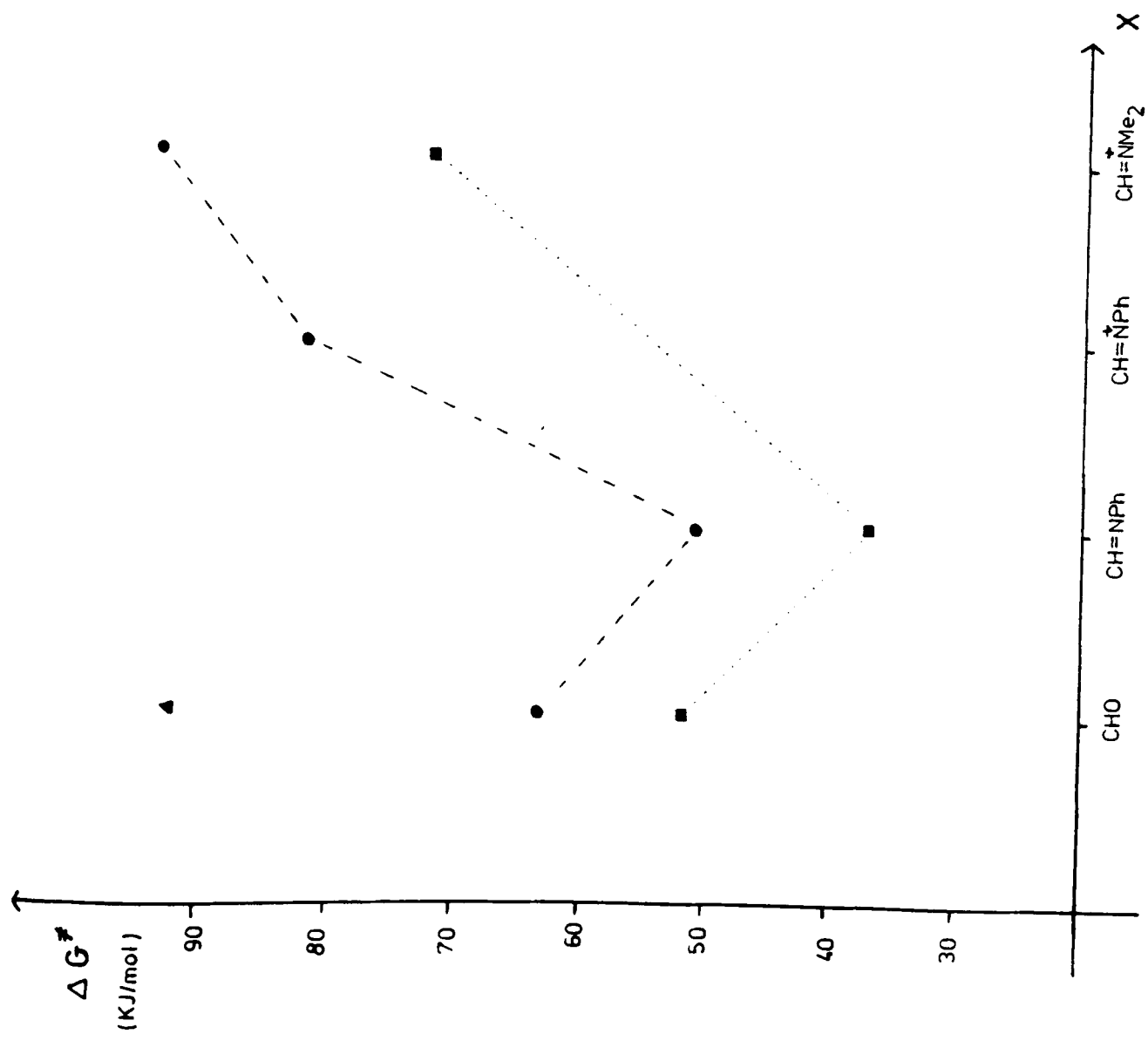
ΔG^\ddagger Values for Dimethylaminoacrolein, Measured in Both d_6 -Acetone and d_6 -D.M.S.O.

Table 8

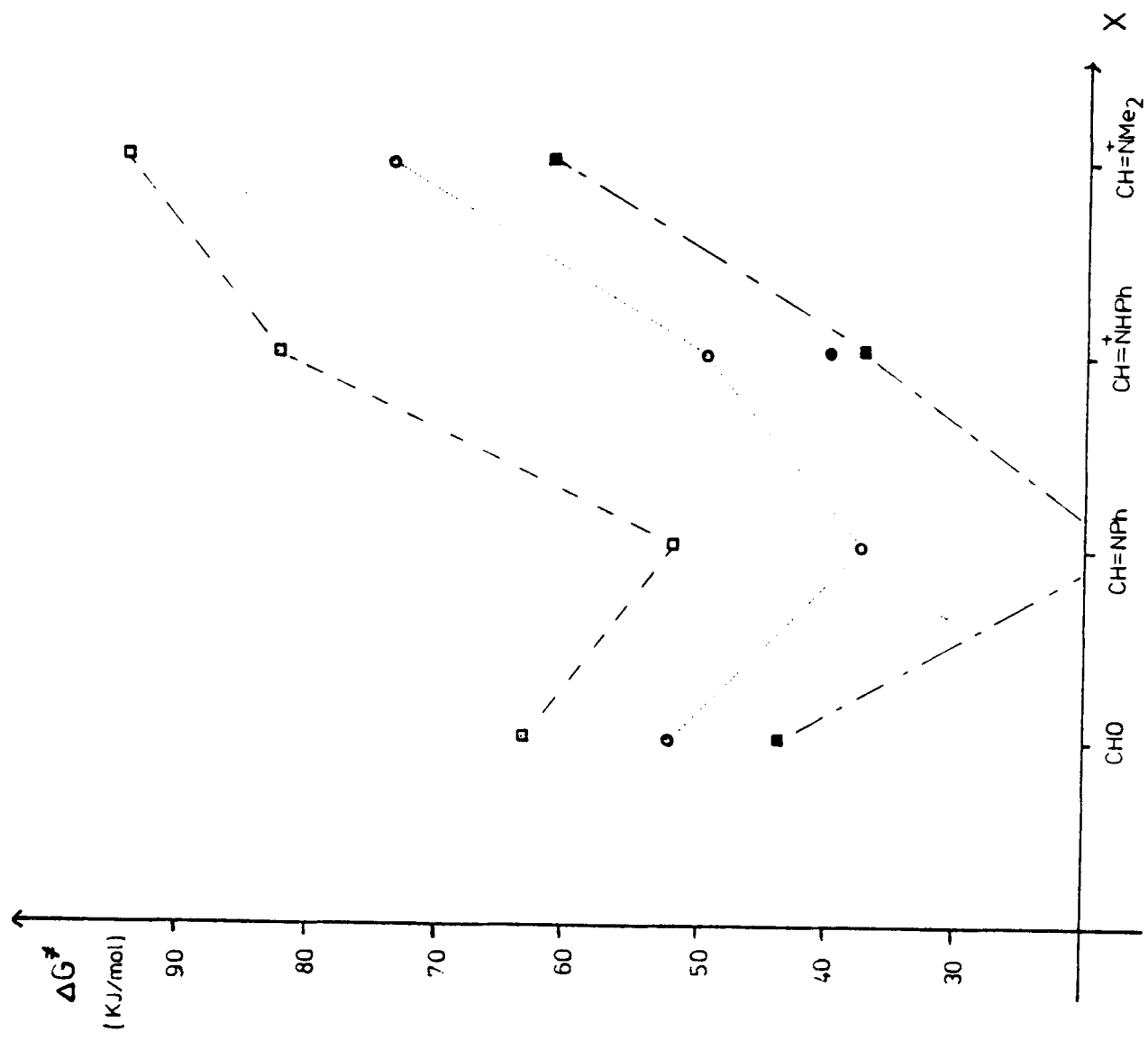
The effect of varying the X substituent is shown in Graph 1 and Tables 9 and 11 for all three series studied. It appears that rotation of the dimethylamino group is most facile when X=N-phenyl and least facile for the quaternary salts. The two other examples studied are found in intermediate positions, although the position of the anilinium salt is rather variable.



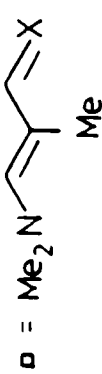
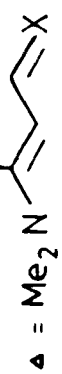
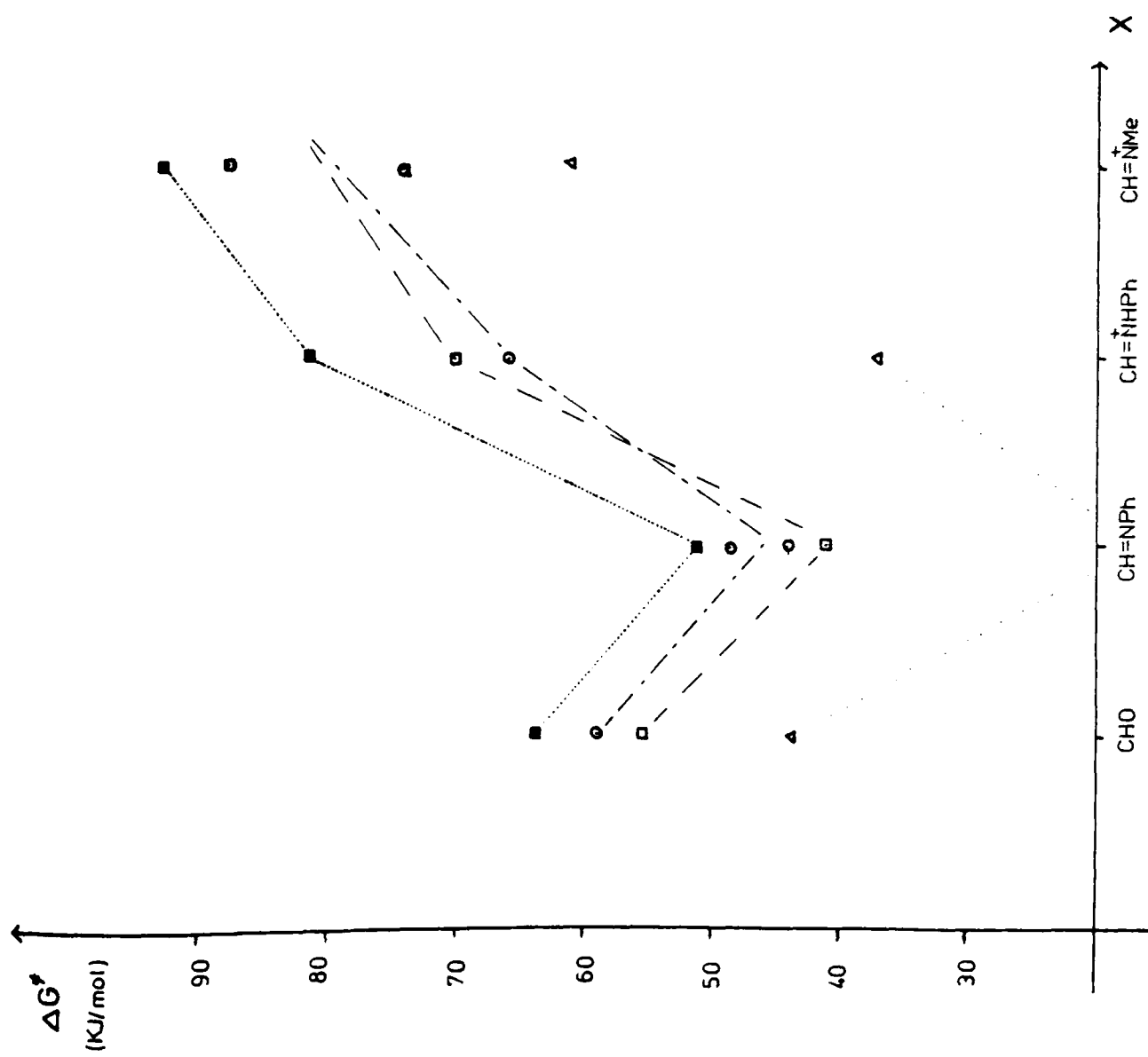
These results can be explained by the ability of the X group to stabilise canonical form (B). The quaternary salt (139), for example, exists as a 50:50 mixture of canonical forms (A) and (B) whereas the N-phenyl substituted analogue (76) exists mainly as canonical form (A). Similarly for (140), the oxygen substituted analogue, canonical form (A) predominates,



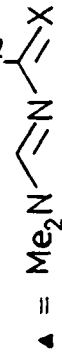
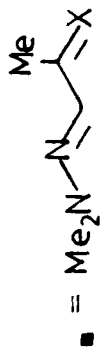
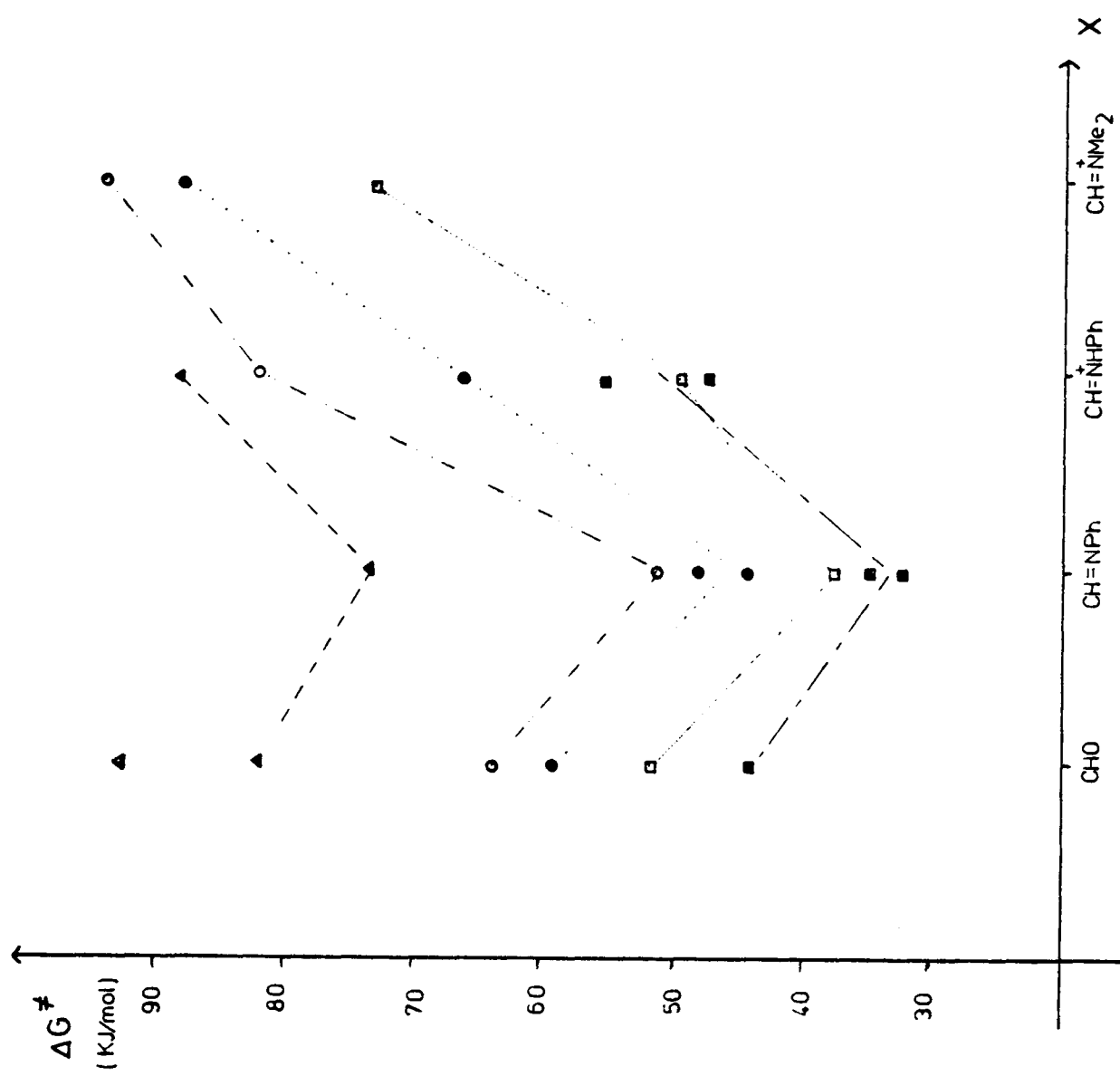
Graph 1



Graph 2



Graph 3



Graph 4

ΔG^\ddagger Values obtained by Variable Temperature ^1H N.M.R.

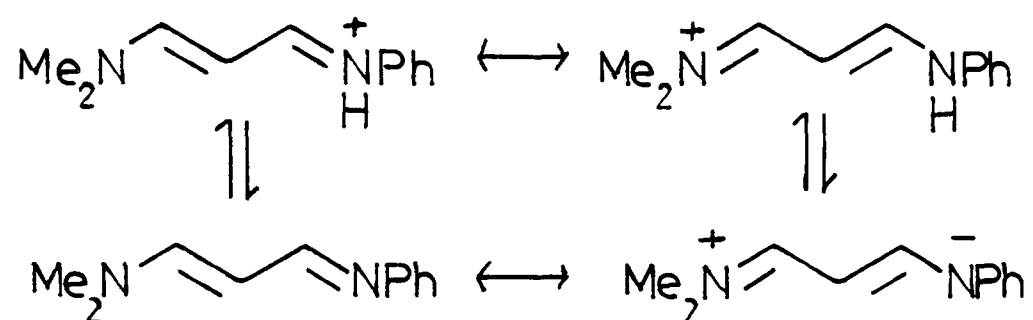
Spectroscopy:

		O	NPh	(+) NPh H	(+) NMe ₂	S
	(i)	51.8	37.5	49.6	73.1 >92.9	-
	(ii)	<	<	40.0	-	-
	(iii)	44.51	35.14 32.68	47.51 55.58	-	-
	(iv)	64.0	51.4	82.2	93.5	-
	(v)	55.68	41.32	70.64	74.47 88.04	-
	(vi)	43.9	<	37.5	61.7	-
	(vii)	59.30	44.53 48.11	66.5	74.47 88.04	-
	(viii)	92.5	-	-	>	-
	(ix)	81.88	73.49	88.03	-	-
	(x)	84.55	-	-	-	90.35

Table 9

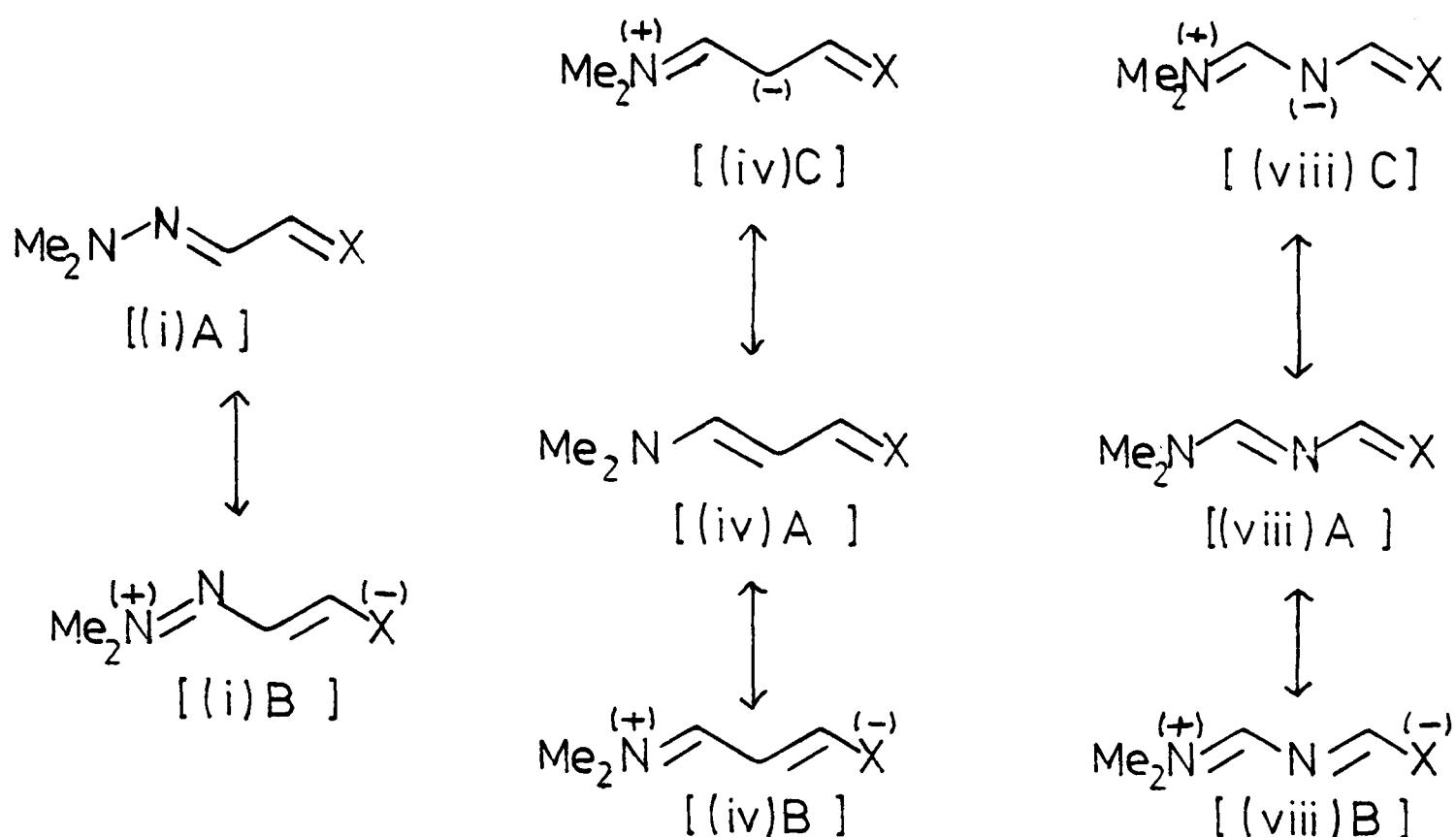
although a higher proportion of (B) is present than for (76) due to the greater electronegativity of oxygen compared to nitrogen. Thus, the relative barriers to rotation of $X=O$, $X=NPh$ and $X=\overset{+}{N}Me_2$ compounds are readily explained.

The anilinium salt ($X=\overset{+}{N}HPh$) is almost certainly in equilibrium with its base.



The free base has a much lower barrier to rotation than its protonated salt, therefore the anilinium salt has two factors affecting the rotation of the dimethylamine group; the canonical forms and the equilibrium. The equilibrium is compound dependent, varying with the acidic nature of the different salts and therefore accounts for the variable ΔG^\ddagger values obtained for these compounds.

Placing a nitrogen in the pentadiene chain is shown to affect the energetics of the dimethylamino rotation process. It can be seen from Graph 1 and Tables 9 and 11 that a nitrogen in the 2-position [(i) series] allows more facile rotation of the dimethylamino group relative to series (iv) and (viii). This is presumably because the canonical form [(i)B] is disfavoured due to the positive charge being carried by the atom adjacent to the aza nitrogen compared with [(iv)B]. In turn, canonical form [(viii)C] is favoured more



than the analogous canonical form [(iv)C], due to the greater electronegativity of the nitrogen atom in comparison with the carbon atom. Hence series (viii) shows more restricted rotation of the dimethylamino group and therefore higher ΔG^\ddagger values.

When a central methyl group is placed on the pentadiene chain, Graph 2, Tables 9 and 11, the ΔG^\ddagger values are very much reduced. However, there is not enough data for the 3-methyl-1,2,5-triazapentadiene series where the ΔG^\ddagger values were either very low or the compounds not obtainable. It was thought possible that one explanation of the low ΔG^\ddagger values obtained for these compounds could be the possibility of the molecule being partially twisted due to the interaction of the central methyl group and one of the N-methyl groups. To test this prediction, an X-ray structure of (144) was obtained (Table 10).

Table 10Bond Lengths of (144)

C(11) - N(1)	1.476(8)
C(12) - N(1)	1.461(5)
N(1) - C(2)	1.312(4)
C(2) - C(3)	1.389(4)
C(3) -C(31)	1.525(7)
C(3) - C(4)	1.390(4)
C(4) - N(5)	1.314(4)
N(5) -C(51)	1.465(7)
N(5) -C(52)	1.456(6)
C(1P) -C(2P)	1.462(5)
C(1P) -C(6P)	1.446(4)
C(1P) - O(1)	1.228(4)
C(2P) -C(3P)	1.361(5)
C(2P) -N(2P)	1.463(5)

C(3P) -C(4P)	1.367(4)
C(4P) -C(5P)	1.389(5)
C(4P) -N(4P)	1.439(4)
C(5P) -C(6P)	1.365(5)
C(6P) -N(6P)	1.449(4)
N(2P) -O(21)	1.224(5)
N(2P) -O(22)	1.189(6)
N(2P) -O(21A)	1.23(3)
N(2P) -O(22A)	1.19(5)
N(4P) -O(41)	1.224(4)
N(4P) -O(42)	1.226(4)
N(6P) -O(61)	1.208(5)
N(6P) -O(62)	1.197(5)

Bond Angles of (144)

C(11) - N(1) -C(12)	114.1(4)
C(11) - N(1) - C(2)	125.2(4)
C(12) - N(1) - C(2)	120.7(3)
N(1) - C(2) - C(3)	131.4(3)
C(2) - C(3) -C(31)	123.8(3)
C(2) - C(3) - C(4)	111.8(3)
C(31) - C(3) - C(4)	123.7(3)
C(3) - C(4) - N(5)	131.5(3)
C(4) - N(5) -C(51)	125.3(3)
C(4) - N(5) -C(52)	120.1(3)
C(51) - N(5) -C(52)	114.6(4)
C(2P) -C(1P) -C(6P)	110.8(3)
C(2P) -C(1P) - O(1)	123.9(3)
C(6P) -C(1P) - O(1)	125.2(3)
C(1P) -C(2P) -C(3P)	125.0(3)
C(1P) -C(2P) -N(2P)	119.0(3)
C(3P) -C(2P) -N(2P)	116.0(3)
C(2P) -C(3P) -C(4P)	119.2(3)
C(3P) -C(4P) -C(5P)	120.9(3)

C(3P) -C(4P) -N(4P)	119.3(3)
C(5P) -C(4P) -N(4P)	119.8(3)
C(4P) -C(5P) -C(6P)	119.7(3)
C(1P) -C(6P) -C(5P)	124.3(3)
C(1P) -C(6P) -N(6P)	119.6(3)
C(5P) -C(6P) -N(6P)	116.1(3)
C(2P) -N(2P) -O(21)	118.1(4)
C(2P) -N(2P) -O(22)	120.5(4)
C(2P) -N(2P) -O(21A)	118.0(15)
C(2P) -N(2P) -O(22A)	120.3(22)
O(21) -N(2P) -O(22)	121.4(4)
O(21A) -N(2P) -O(22A)	121.6(27)
C(4P) -N(4P) -O(41)	117.9(3)
C(4P) -N(4P) -O(42)	119.0(3)
O(41) -N(4P) -O(42)	123.1(3)
C(6P) -N(6P) -O(61)	119.8(3)
C(6P) -N(6P) -O(62)	118.9(3)
O(61) -N(6P) -O(62)	121.2(4)

Table 10 (continued)Torsion Angles of (144)

C(11)	-	N(1)	-	C(2)	-	C(3)	-7.0(6)
C(12)	-	N(1)	-	C(2)	-	C(3)	173.2(4)
N(1)	-	C(2)	-	C(3)	-	C(31)	-9.8(6)
N(1)	-	C(2)	-	C(3)	-	C(4)	179.8(3)
C(2)	-	C(3)	-	C(4)	-	N(5)	-179.7(3)
C(31)	-	C(3)	-	C(4)	-	N(5)	9.9(6)
C(3)	-	C(4)	-	N(5)	-	C(51)	9.2(6)
C(3)	-	C(4)	-	N(5)	-	C(52)	-169.5(4)
C(6P)	-	C(1P)	-	C(2P)	-	C(3P)	-4.4(5)
C(6P)	-	C(1P)	-	C(2P)	-	N(2P)	176.2(3)
O(1)	-	C(1P)	-	C(2P)	-	C(3P)	172.9(3)
O(1)	-	C(1P)	-	C(2P)	-	N(2P)	-6.5(5)
C(2P)	-	C(1P)	-	C(6P)	-	C(5P)	3.9(4)
C(2P)	-	C(1P)	-	C(6P)	-	N(6P)	-177.7(3)
O(1)	-	C(1P)	-	C(6P)	-	C(5P)	-173.4(3)
O(1)	-	C(1P)	-	C(6P)	-	N(6P)	5.1(5)
C(1P)	-	C(2P)	-	C(3P)	-	C(4P)	2.7(5)
N(2P)	-	C(2P)	-	C(3P)	-	C(4P)	-177.9(3)
C(1P)	-	C(2P)	-	N(2P)	-	O(21)	151.6(4)
C(1P)	-	C(2P)	-	N(2P)	-	O(22)	-26.2(5)
C(1P)	-	C(2P)	-	N(2P)	-	O(21A)	-146.1(17)
C(1P)	-	C(2P)	-	N(2P)	-	O(22A)	37.1(26)
C(3P)	-	C(2P)	-	N(2P)	-	O(21)	-27.8(5)
C(3P)	-	C(2P)	-	N(2P)	-	O(22)	154.4(4)
C(3P)	-	C(2P)	-	N(2P)	-	O(21A)	34.5(17)
C(3P)	-	C(2P)	-	N(2P)	-	O(22A)	-142.4(26)
C(2P)	-	C(3P)	-	C(4P)	-	C(5P)	0.1(5)
C(2P)	-	C(3P)	-	C(4P)	-	N(4P)	179.3(3)
C(3P)	-	C(4P)	-	C(5P)	-	C(6P)	-0.6(5)
N(4P)	-	C(4P)	-	C(5P)	-	C(6P)	-179.8(3)
C(3P)	-	C(4P)	-	N(4P)	-	O(41)	-177.5(3)
C(3P)	-	C(4P)	-	N(4P)	-	O(42)	3.8(5)
C(5P)	-	C(4P)	-	N(4P)	-	O(41)	1.7(5)
C(5P)	-	C(4P)	-	N(4P)	-	O(42)	-177.0(3)
C(4P)	-	C(5P)	-	C(6P)	-	C(1P)	-1.6(5)
C(4P)	-	C(5P)	-	C(6P)	-	N(6P)	179.9(3)
C(1P)	-	C(6P)	-	N(6P)	-	O(61)	-166.4(3)
C(1P)	-	C(6P)	-	N(6P)	-	O(62)	16.3(5)
C(5P)	-	C(6P)	-	N(6P)	-	O(61)	12.2(5)
C(5P)	-	C(6P)	-	N(6P)	-	O(62)	-165.1(4)

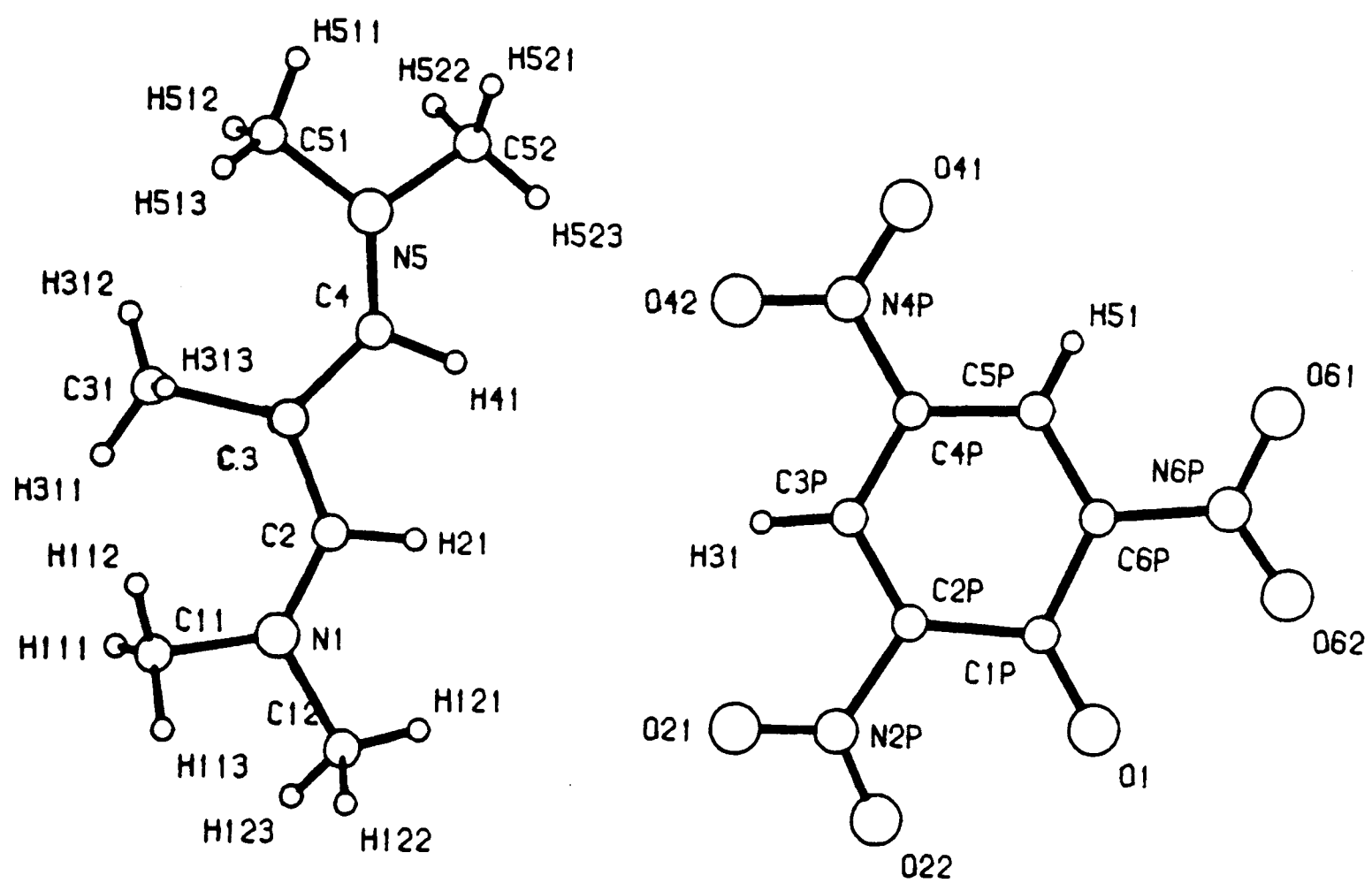
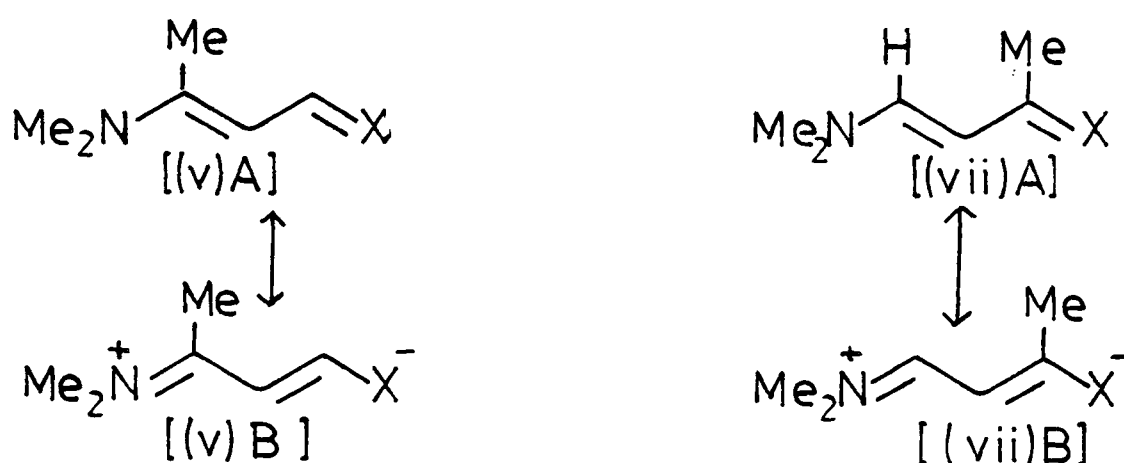


Figure 1: Numbering system for (144) and the picrate anion

The molecular conformations were defined by the four torsion angles: $C(12)-N(1)-C(2)-C(3) = 173.2(4)^\circ$, $N(1)-C(2)-C(3)-C(4) = 179.8(3)^\circ$, $C(52)-N(5)-C(4)-C(3) = 169.5(4)^\circ$, $N(5)-C(4)-C(3)-C(2) = -179.7(3)^\circ$ and surprisingly showed a twist about both terminal C-N bonds of around only 10° from a trans-planar conformation. Nevertheless, this is more than is observed in related structures without the central methyl group¹⁵⁷. Only a small twist is therefore required to relieve steric interaction between the short Me ... Me contacts. A more notable feature of the structure of (144) obtained from the X-ray data is the effect of steric repulsion between the methyl group at C(11), C(31) and C(51) to give exceptionally wide bond angles at C(2) and C(4) of 131° .¹⁵⁸ Those bond angles would normally be expected to be in the range of $120-125^\circ$.¹⁵⁹

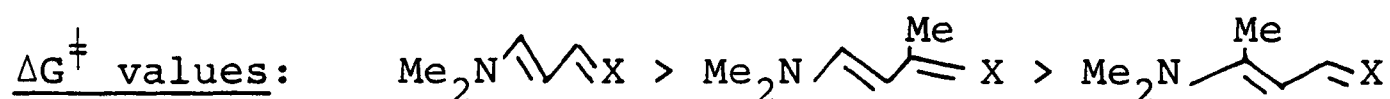
Perhaps this increase in bond angles leads to a less efficient overlap of the p orbitals in the π system. The reduced overlap of the p orbitals elongates the π system and weakens conjugation thereby allowing rotation about the C-N bond to take place more freely. Alternatively, it may be that the 10° twist of the molecule is sufficient to considerably reduce the ΔG^\ddagger values.

When there is a methyl group placed at the 2- or 4-position of the pentadiene chain, a reduction in ΔG^\ddagger value is found, however the effect is much less than the corresponding central methyl group series. The ΔG^\ddagger values are reduced most when the methyl group is placed on the carbon adjacent to the dimethylamino group. The electron donating group might have



been expected to stabilise canonical form [(v)B] but obviously this is not the case. Instead, geometric factors due to the bulky methyl group must be accounting for the lowering of the ΔG^\ddagger values.

When the methyl group is placed as far away from the dimethylamino group as possible, i.e. on C(4), the ΔG^\ddagger values are between the unsubstituted analogues and the C(2) methyl substituted compounds:

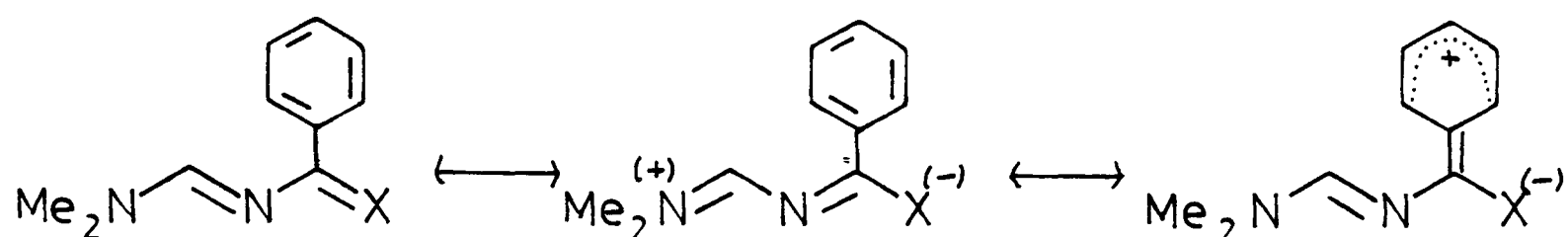


It is possible that with series (vii), the methyl group at the C(4) position may be destabilising canonical form [(vii)B] due to its electron donating effect. Steric interaction of the methyl in the 4-position and the hydrogen atom in the 2-position can be ruled out since the effect is also shown in the 1,2,5-triazapentadiene series in which there is no hydrogen in the 2-position.

The effect of a sulphur atom at position X was demonstrated by comparing the phenyl substituted compounds (118) and (119).

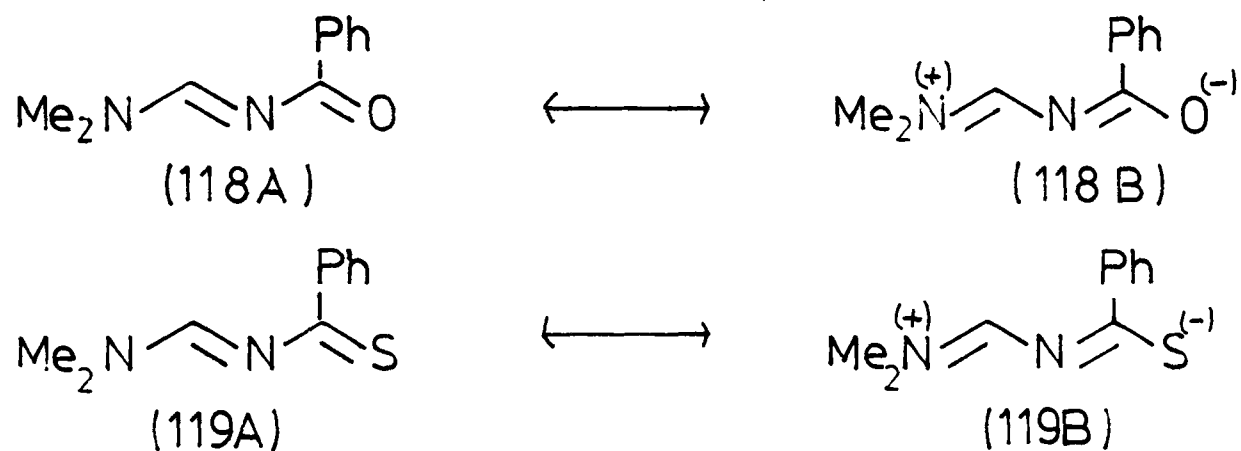
As mentioned previously, it was not possible to prepare a thio compound in this series, with a methyl at C(4). The results obtained for (119) were compared with the analogous oxygen compound (118).

The phenyl group on C(4) of the pentadiene chain appears to reduce the ΔG^\ddagger values in comparison with the unsubstituted analogues. This may be because of the electronic effects on



the phenyl group. The C(2) methyl substituted analogues have even lower ΔG^\ddagger values as was discussed previously.

Comparison of compounds (118) and (119) showed a higher



ΔG^\ddagger value for the sulphur containing diene. This is probably due to the high polarity of this ^{thio}carbonyl, favouring canonical form (119B) and so hindering rotation about the C-N bond.

Table 11

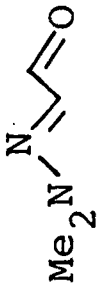
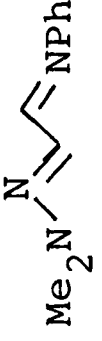
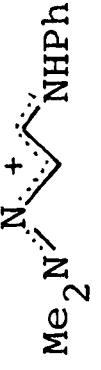

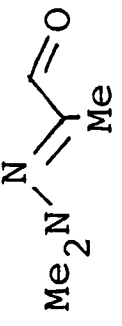
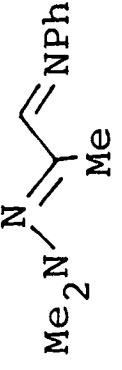
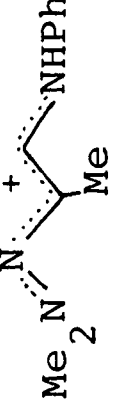
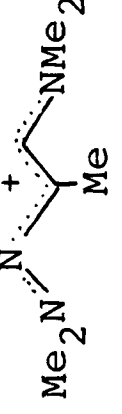
Series	Compound	Cmpd. No.	Solvent	$\Delta\nu$ (Hz)	T_c ($^{\circ}\text{K}$)	ΔG^{\ddagger} (KJmol^{-1})
(i)		(145)	d ₆ -acetone	75.22	258	51.8
(i)		(146)	d ₆ -acetone	58.69	187	37.5
(i)		(147)	d ₆ -acetone	66.89	246	49.6
(i)		(148)	d ₆ -d.m.s.o. d ₆ -d.m.s.o.	60.33 24.45	356 >433	73.1 >92.9
(ii)		(136)	d ₆ -acetone	-	<176	-
(ii)		(138)	d ₆ -acetone	-	<169	-
(ii)		(137)	D ₆ -acetone	26.65	193	40.0
(ii)		-		-	-	-

Table 11 (continued)


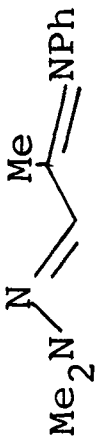
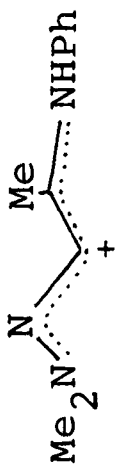
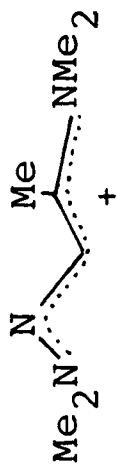




Series	Compound	Cmpd. No.	Solvent	$\Delta\nu$ (Hz)	T_C ($^{\circ}\text{K}$)	ΔG^{\ddagger} (KJmol^{-1})
(iii)		(149)	d ₆ -acetone	76.50	223	44.51
(iii)		(150)	d ₆ -acetone	120.0	181	35.14
(iii)		(151)	d ₆ -acetone	92.0	167	32.68
(iii)		-	-	-	-	-
(iv)		(140)	d ₆ -acetone	63.66	314	64.0
(iv)		(76)	d ₆ -acetone	50.77	252	51.4
(iv)		(75)	d ₆ -d.m.s.o.	40.22	392	82.2
(iv)		(139)	d ₆ -d.m.s.o.	35.78	442	93.5

Table 11 (continued)

Series	Compound	Cmpd. No.	Solvent	$\Delta\nu$ (Hz)	T _c (°K)	ΔG^\ddagger (KJmol ⁻¹)
(v)		(93)	d ₆ -acetone	42.91	268	55.68
(v)		(95)	d ₆ -acetone	38.20	202	41.32
(v)		(94)	d ₆ -d.m.s.o.	8.25	319.5	70.64
(v)		(92)	d ₆ -d.m.s.o.	13.24	342	74.47
				47.01	385	88.04
(vi)		(141)	d ₆ -acetone	13.68	206	43.9
(vi)		(85)	d ₆ -acetone	-	<<183	-
(vi)		(84)	d ₆ -acetone	18.80	177	37.5
(vi)		(144)	d ₆ -acetone	16.18	287.5	61.7

Table 11 (continued)

Series	Compound	Cmpd. No.	Solvent	$\Delta\nu$ (Hz)	T_C (°K)	ΔG^\ddagger (KJmol ⁻¹)
(vii)		(94)	d ₆ -acetone	66.12	292	59.30
(vii)		(91)	d ₆ -acetone	112.44	221	44.53
(vii)		(90)	d ₆ -acetone	60.44	244	48.11
(vii)		(92)	d ₆ -d.m.s.o.	102.11	331	66.50
			d ₆ -d.m.s.o.	13.24	342	74.47
			d ₆ -d.m.s.o.	47.01	385	88.04
(viii)		(152)	d ₆ -d.m.s.o.	29.2	434	92.5
(viii)			-	-	-	-
(viii)			-	-	-	-
(viii)		(153)	d ₆ -d.m.s.o.	18.03	>413	-

Table 11 (continued)

Series	Compound	Cmpd. No.	Solvent	$\Delta\nu$ (Hz)	T _C (°K)	ΔG^\ddagger (KJmol ⁻¹)
(ix)		(116)	d ₆ -d.m.s.o.	10.06	371	81.88
(ix)		(125)	d ₆ -d.m.s.o.	25.50	346	73.49
(ix)		(154)	d ₆ -d.m.s.o.	7.27	418	88.03
(ix)		-	-	-	-	-
(x)		(118)	d ₆ -d.m.s.o.	9.60	382	84.55
(x)		(119)	d ₆ -d.m.s.o.	19.38	417	90.35

EXPERIMENTAL

Symbols and Abbreviations

b.p.	boiling point
m.p.	melting point
t.l.c.	thin layer chromatography
g.c.	gas-liquid chromatography
g.c./m.s.	gas-liquid chromatography/mass spectrometry
n.m.r.	nuclear magnetic resonance
br	broad
s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet
δ	chemical shift
U.V.	ultra-violet
i.r.	infra red
ν	wavenumber
m.s.	mass spectrometry
M^+	mass of molecular ion
m/z	mass to charge ratio
h	hours
min	minutes
mol	moles
mmol	millimoles

Instrumentation

Mass Spectrometry. Mass spectra were recorded by Mr. D. Thomas and latterly by Mr. A. Thomson on an AEI MS902 mass spectrometer.

Nuclear Magnetic Resonance Spectrometry

(i) ^1H n.m.r. spectra were recorded mainly by Mr. J.R.A. Millar on a Varian HA100 or by Mr. L.H. Bell on a Bruker WP80 spectrometer. High field ^1H n.m.r. spectra were recorded by Dr. D. Reed on a Bruker WH360 spectrometer and variable temperature ^1H n.m.r. spectra were recorded by Mr. J.R.A. Millar on a Bruker WP200 instrument. Chemical shifts (δ_{H}) are measured in parts per million relative to tetramethylsilane ($\delta = 0.0$) or chloroform ($\delta = 7.25$).

(ii) ^2H n.m.r. spectra were recorded by Dr. D. Reed on a Bruker WH360 spectrometer. Chemical shifts (δ_{D}) are measured in parts per million relative to tetramethylsilane ($\delta = 0.0$).

(iii) ^{13}C n.m.r. spectra were recorded by Mr. J.R.A. Millar and Miss E. Stevenson on a Varian CFT20 spectrometer. Chemical shifts (δ_{C}) are measured in parts per million relative to tetramethylsilane ($\delta = 0.0$).

All n.m.r. spectra were recorded for deuteriochloroform solutions unless otherwise stated.

Gas-liquid Chromatography. Qualitative and preparative g.c. were carried out on a Carlo Erba Strumentazione Fractovap 2450 instrument fitted with a flame ionisation detector and with nitrogen used as the carrier gas. Samples for qualitative g.c.

were run on a 2m x 4.5mm column of either 5% Carbowax 20M on Gas-Chrom (80-100 mesh), or 5% SE30 on Gas-Chrom (80-100 mesh). Preparative g.c. was performed on a 0.85m x 12mm column of 10% Carbowax 20M, or 10% SE30, on Chromosorb W (30-60 mesh). G.c./m.s. results were obtained from a Pye series 104 chromatograph coupled to a VG Micromass 12 spectrometer operated by Miss E. Stevenson.

Thin-layer Chromatography. Analytical chromatograms were developed on alumina coated (0.3mm, Merck, neutral aluminium oxide 60G, type E) or silica coated (0.3mm, Merck Type 60G) glass plates, both containing Woelm fluorescent green indicator (0.5%) in the coating. The components were observed under ultra-violet light.

Column Chromatography. Alumina chromatography was carried out using Laporte Industries, Type H alumina which was deactivated by addition of water (6%). Silica chromatography was carried out using Fisons 60-120 mesh 'Silica for Chromatography'.

Elemental Analysis. Microanalyses were obtained using a Perkin Elmer 204 elemental analyser operated by Mr. J. Grunbaum.

Melting Points. Melting points of some new compounds were recorded on a Kofler hot stage microscope. All other melting points were recorded on Gallenkamp or Electrothermal apparatus.

Infra-red Spectroscopy. Spectra were recorded on a Perkin Elmer 157G and latterly on a Perkin Elmer 781 spectrometer. Samples were examined as liquid films or nujol mulls.

Solvents. In general commercially available solvents were used without further purification. Light petroleum, however, was distilled before use, *e.g.* light petroleum (40/60) refers to the fraction boiling at 40-60°C. Dry ether refers to ether dried by, and stored over, sodium wire. Dimethyl sulphoxide was dried over potassium hydroxide.

Pyrolysis Apparatus and General Techniques

Flash vacuum pyrolysis was mainly carried out on apparatus based on the design of W.D. Crow, Australian National University. The important features of this apparatus are shown in Figure 2. The sample was volatilised from a horizontal inlet tube, heated by a Buchi Kugelrohr oven, into a silica furnace tube (30 x 2.5cm). This was maintained at temperatures in the range 600-900°C by a Stanton Redcroft laboratory tube furnace LM8100, the temperature being measured by a platinum/platinum 13% rhodium thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen and situated at the exit point of the furnace. The apparatus was evacuated to 10^{-2} - 10^{-3} Torr by an Edwards Model ED100 high capacity rotary oil pump, the pressure being measured by a McLeod gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1-10 milliseconds.

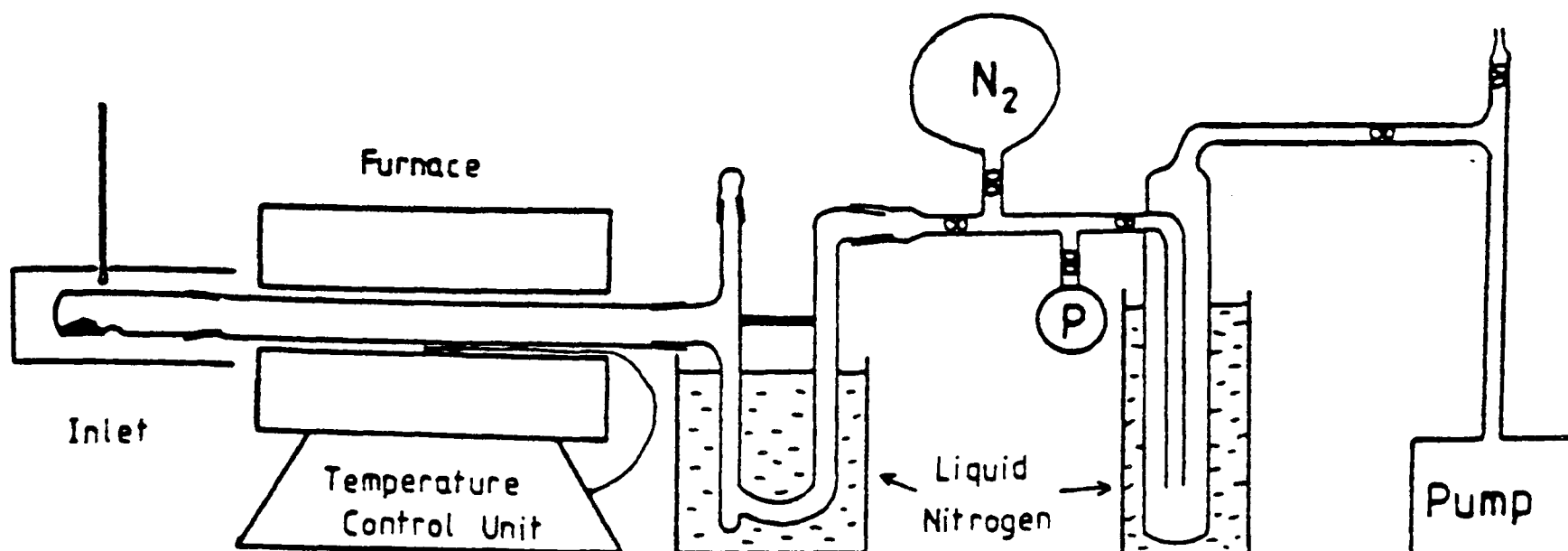


Figure 2

In some examples however, it was not possible to volatilise the sample into the furnace from the horizontal inlet tube due to decomposition of the compound on prolonged exposure to high temperatures. In these circumstances a Stanton Redcroft LMVS100 vertical furnace was used to heat a silica furnace tube (30 x 2.5 cm) containing a silica wool plug about half way down as shown in Figure 3. . The sample was held above the furnace, though not directly above the heat, until the correct furnace temperature and pressure were reached. Then the glass sidearm was twisted (*re* arrows in diagram) until the material to be pyrolysed slid down into the furnace.

This type of apparatus was originally designed by Wentrup⁴⁶ and was constructed at Edinburgh University by Mr. G. Smith. It is also a very useful technique for involatile materials that cannot be sublimed into the horizontal furnace in the usual manner.

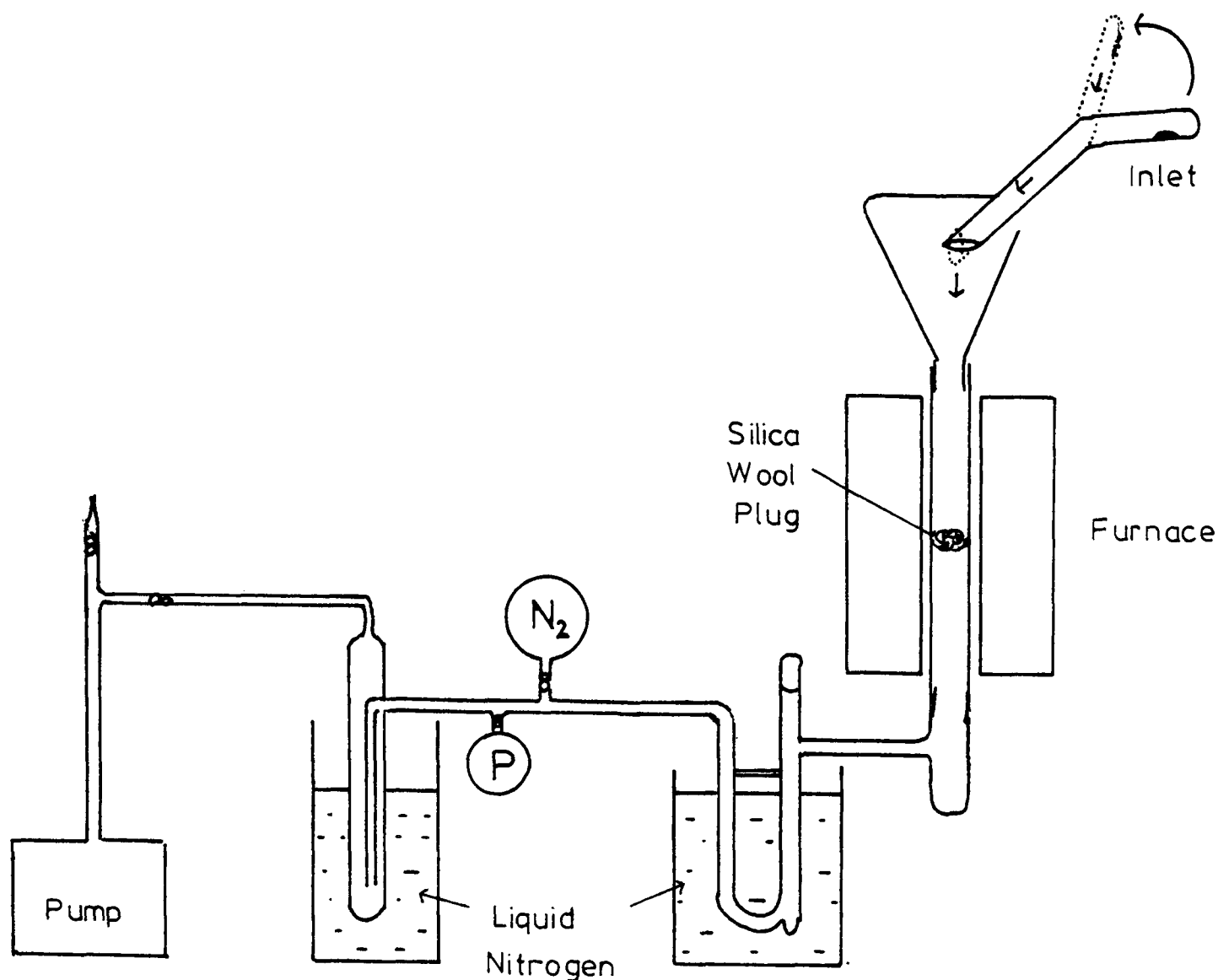


Figure 3

Small scale pyrolyses were generally carried out with sample sizes of 0.2-1.0mmol. The entire pyrolysate was dissolved in deuteriochloroform and analysed by ^1H n.m.r., g.c. and g.c./m.s. Products were characterised by comparison with authentic samples. In most cases two independent methods of identification were used; comparison with an authentic sample by g.c. and comparison of m.s. breakdown patterns obtained by g.c./m.s. In most cases ^1H n.m.r. spectroscopy was also used. Absolute yields were obtained from the ^1H n.m.r. spectra by addition of cyclohexane (5 μl) or methylene chloride (10 μl) as an integral calibrant (yields calculated by this method are estimated to be correct to $\pm 5\%$) or in some

cases by g.c. using an internal standard. Relative yields were normally obtained by g.c. after calibration of the detector response.

For preparative scale experiments sample sizes of 0.5-1.5g were used.

In the sections which deal with pyrolysis experiments the conditions are quoted as follows: substrate, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time and products. However where the vertical furnace was used, the pressure quoted is the initial pressure although the pressure rose as the compounds passed through the furnace. No inlet temperature or pyrolysis time is quoted for the vertical furnace as, generally, the material to be pyrolysed was dropped in one batch through the furnace. Although results were satisfactory, this technique may be improved by a slower input rate.

PART 1PREPARATION AND PYROLYSIS OF 1,5-DIAZAPENTADIENESPREPARATION OF 1,5-DIAZAPENTADIENESPreparation of Methylmalondialdehyde tetraethyldiacetal.-

Triethylorthoformate (40g, 0.27mol) and boron trifluoride (0.13ml) were stirred together under nitrogen at 30°C. Ethyl propenyl ether (17.5g, 0.21mol) was then added dropwise with stirring over 1 hour (keeping the reaction temperature below 40°C). The mixture was stirred for 6h and then left to stand at room temperature overnight. Sodium carbonate (1g, 0.01mol) was added and the mixture was stirred for 1h before the solid was filtered and the filtrate was distilled. The first fraction [b.p. 56-100°C (10 Torr)] was discarded but the second fraction, b.p. 108°C (10 Torr) [lit.¹⁶⁰ 120°C (10 Torr)] gave the required product (28.05g, 57%); δ_H 4.44 (2H, d), 3.8-3.4 (8H, m), 3.04 (1H, q), 1.25-1.1 (12H, m) and 0.94 (3H, d).

Preparation of 1,5-Diaryl-1H-1,5-diazapentadienium perchlorates.-

The perchlorate salts were prepared by the action of the appropriate aniline (0.2mol) on the appropriate 1,3-dicarbonyl compound (0.1mol) (protected as its mono- or di-acetal) in ethanol (10ml), in the presence of perchloric acid (60%, 20ml). The perchlorate salt precipitated immediately (unless otherwise stated) and was filtered off and was washed thoroughly with ether. The following compounds were prepared in this way:
 1,5-diphenyl-1H-1,5-diazapentadienium perchlorate (56%), m.p. 220-222°C (lit.¹⁶¹ m.p. 220-221°C): 1,5-diphenyl-2-methyl-1H-

1,5-diazapentadienium perchlorate. This solution was heated at about 60°C for 1h before ether (150ml) was added to the cooled solution and the mixture was left at -30°C overnight. The crystals were then filtered off as before; 45% m.p. 185-187°C (lit.¹⁶² 185-187°C) δ ([²H₆]acetone) 8.73 (1H, dd), 7.6-7.2 (10H, complex), 6.13 (1H, d) and 2.78 (3H, s): 1,5-diphenyl-3-methyl-1H-1,5-diazapentadienium perchlorate - (67%), m.p. 250-252°C (from aqueous ethanol/acetone) (Found: C, 56.9; H, 5.0; N, 8.35. C₁₆H₁₇ClN₂O₄ requires C, 57.05; N, 5.1; N, 8.3%); δ _H ([²H₆] D.M.S.O.) 11.12 (2H, d), 8.58 (2H, d), 7.1-7.6 (10H, m), and 2.09 (3H, s): 1,5-di([²H₅]phenyl)-1H-1,5-diazapentadienium perchlorate (93%) from [²H₅]aniline: 1,5-di-o-tolyl-1H-1,5-diazapentadienium perchlorate - (84%), m.p. 209-211°C (from ethanol) (Found: C, 58.65; H, 5.4; N, 7.75. C₁₇H₁₉ClN₂O₄ requires C, 58.2; H, 5.4; N, 8.0%); δ _H ([²H₆]acetone) 10.7 (br), 8.3-8.9 (2H, m), 7.2-7.6 (8H, m), 6.59 and 6.01 (1H, 2t), and 2.40, 2.36 and 2.32 (6H, 3s): two isomers were present in a 6:4 ratio, with the major isomer reported first.

Preparation of 1,1-Dialkyl-5-phenyl-1H-1,5-diazapentadienium perchlorates.- The appropriate 1,5-diphenyl-1H-1,5-diazapentadienium perchlorate (20mmol) was suspended in methanol (10ml) and the appropriate dialkylamine (40mmol) was added. The perchlorate salt dissolved as the flask was swirled. The solution was set aside for 5 minutes after which time the product usually crystallised. Ether (100ml) was added and the product was filtered and was washed with dilute hydrochloric acid (1M, 2 x 25ml) and then with water (25ml). The

following compounds were prepared by this method:

1,1-dimethyl-5-phenyl-1H-1,5-diazapentadienium perchlorate,

(62%), m.p. 155-157°C (from aqueous ethanol) (Found: C, 47.65; H, 5.9; N, 9.9. $C_{11}H_{16}ClN_2O_4$ requires C, 47.9; H, 5.85; N, 10.15%); δ_H ($[^2H_6]$ acetone) 8.55 (1H, dd), 8.08 (1H, d), 7.5-7.1 (5H, m), 5.98 (1H, t), 3.40 (3H, s) and 3.18 (3H, s):

1,1-diethyl-5-phenyl-1H-1,5-diazapentadienium perchlorate,

this compound precipitated on the addition of ether, after the solution had been set aside overnight; (73%), m.p. 142-144°C (from aqueous ethanol) (Found: C, 51.3; H, 6.4; N, 9.25.

$C_{13}H_{20}ClN_2O_4$ requires C, 51.4; H, 6.65; N, 9.2%); δ_H ($[^2H_6]$ -acetone) 8.54 (1H, d), 8.18 (1H, d), 7.5-7.2 (5H, m), 6.14

(1H, t), 3.67 (4H, t) and 1.32 (6H, q): 1-ethyl-1-methyl-5-phenyl-1H-1,5-diazapentadienium perchlorate, (79%), m.p. 128-

130°C (from isopropyl alcohol) (Found: C, 50.15; H, 5.9;

N, 9.9. $C_{12}H_{17}ClN_2O_4$ requires C, 49.9; H, 5.9; N, 9.7%).

1H n.m.r. showed two isomers to be present, the major isomer is recorded first - δ_H ($[^2H_6]$ acetone) 8.50 (1H, br d), 8.24, 8.12 (1H, d), 7.5-7.2 (5H, m), 6.03, 6.14 (1H, t), 3.71, 3.63 (2H, q), 3.23, 3.45 (3H, s) and 1.35, 1.28 (3H, t):

1-isopropyl-1-methyl-5-phenyl-1H-1,5-diazapentadienium per-
chlorate, (75%), m.p. 112-114°C (from ethanol) (Found: C, 51.4;

H, 6.3; N, 9.3. $C_{13}H_{19}ClN_2O_4$ requires C, 51.55; H, 6.3;

N, 9.3%). The aliphatic resonances in the 1H n.m.r. spectrum, suggested that two isomers were present in a 7:3 ratio and

where appropriate the signal of the major isomer is recorded

first, δ_H ($[^2H_6]$ acetone), 8.56 (1H, d), 8.29 (1H, d), 7.4-7.2

(5H, m), 6.05 (1H, t), 5.74 (1H, br s), 4.05, 3.51 (1H, septet),

3.19, 2.88 (3H, s) and 1.38, 1.42 (6H, d): 5-phenyl-1,1,4-

trimethyl-1H-1,5-diazapentadienium perchlorate, 81%, m.p.

165-167°C (from ethanol) (Found: C, 50.0; H, 6.0; N, 9.85.

$C_{12}H_{18}ClN_2O_4$ requires C, 49.75, H, 6.25, N, 9.65%); δ_H ($[^2H_6]$ -acetone) 8.21 (1H, d), 7.6-7.2 (5H, m), 5.35 (1H, d), 3.32

(6H, br s) and 2.94 (3H, s): 5-phenyl-1,1,3-trimethyl-1H-1,5-

diazapentadienium perchlorate, 60%, m.p. 204-206°C (from

aqueous ethanol) (Found: C, 50.15; H, 5.8; N, 9.45.

$C_{12}H_{17}ClN_2O_4$ requires C, 49.9; H, 5.95; N, 9.2%); δ_H

($[^2H_6]$ D.M.S.O.) 8.38 (1H, s), 8.15 (1H, s), 7.3-6.9 (10H, m),

4.05br (1H, s) ^{3.23 (6H, s),} and 1.90 (3H, s).

Attempted Preparation of 1,1-Diisopropyl-5-phenyl-1H-1,5-diaza-
pentadienium perchlorate. The general method used for the

preparation of 1,1-dialkyl-5-phenyl-1H-1,5-diazapentadienium perchlorates was tried but did not give the required product even after the mixture was heated under reflux for 6h.

Preparation of 5-Phenyl-1,1,2-trimethyl-1H-1,5-diazapentadienium
perchlorate.

(a) 1,1,2,5,5-Pentamethyl-1H-1,5-diazapentadienium perchlorate.-

1,5-Diphenyl-2-methyl-1H-1,5-diazapentadienium perchlorate

(6.73 g, 20mmol) was suspended in methanol (10ml) and an excess of dimethylamine (6.8g, 10ml, 150mmol) was added. The mixture

was stirred overnight then ether (150ml) was added and the

product precipitated out as a pink solid (4.29g, 90%) m.p. 162-163°C (from aqueous ethanol) (lit.¹⁶³ m.p. 154-155°C) (Found:

C, 39.9; H, 7.1; N, 11.65. $C_8H_{17}ClN_2O_4$ requires C, 40.15;

H, 7.15; N, 11.55%). δ_H ($[^2H_6]$ D.M.S.O.) 8.05 (1H, d), 5.19

(1H, d), 3.29 (3H, s), 3.27 (3H, s), 3.20 (3H, s), 3.05 (3H, s) and 2.29 (3H, s).

(b) 3-(Dimethylamino)-3-methylacrolein.- 1,1,2,5,5-Pentamethyl-1H-1,5-diazapentadienium perchlorate was hydrolysed using the general method of Arnold.¹⁶⁴ The perchlorate salt (18.0g, 75mmol) was suspended in water (200ml), treated with a solution of potassium hydroxide (21.0g, 375mmol) in water (200ml) and the mixture was stirred for 2h at room temperature. The precipitated potassium perchlorate was filtered and solid potassium carbonate was added to the filtrate. The resulting solution was extracted with methylene chloride (6x75ml), the combined organic extracts were dried (Na₂SO₄) and the solvent was removed *in vacuo*. The crude product was then purified by bulb to bulb distillation [b.p. 80-82°C (0.1 Torr)] to give a yellow solid which became liquid on standing (6.8g, 80%). This liquid was shown by ¹H n.m.r. to be a mixture of the required aldehyde and its 1-methyl isomer in a 2:1 ratio. The major product is reported first δ_H 9.48 (1H, d), 5.15 (1H, d), 3.02 (6H, s), 2.28 (3H, s), δ_H 7.44 (1H, d), 5.00 (1H, d), 2.96 (6H, s) and 2.08 (3H, s).

(c) 5-Phenyl-1,1,2-trimethyl-1H-1,5-diazapentadienium perchlorate.- Anilinium perchlorate¹⁵⁰ (1.28g, 6.7mmol) was dissolved in ethanol (4ml) and added to a solution of the aldehyde/ketone mixture [1.13g, 6.7mmol (aldehyde), 3.3mmol (ketone)] in ethanol (2ml). A yellow solid precipitated immediately (1.34g, 70%, based on amount of aldehyde) m.p. 216-218°C (from aqueous ethanol) (Found: C, 49.7; H, 5.8; N, 9.45. C₁₂H₁₇ClN₂O₄ requires C, 49.9; H, 5.9; N, 9.7%); δ_H ([²H₆]D.M.S.O.) 8.79 (1H, t),

7.8-7.6 (5H, m), 7.18 (1H, d), 3.67 (3H, s), 3.58 (3H, s) and 2.78 (3H, s).

Preparation of 1,5-Diazapentadienes.- The corresponding perchlorate salt (10mmol) was suspended in a solution of sodium hydroxide (30mmol) in water (20ml). The mixture was extracted into ether (3x30ml) with vigorous shaking, the combined organic extracts were dried (Na_2SO_4) and the ether was removed *in vacuo*. The crude product was purified by bulb to bulb distillation. The following compounds were made using this general procedure.

1,1-Dimethyl-5-phenyl-1,5-diazapentadiene (84%) b.p. 152-155°C (0.1 Torr) (lit.¹¹⁰ m.p. 62-65°C); this compound was fully characterised because of the discrepancy with the literature value. (Found: C, 75.85; H, 8.05; N, 16.1. $\text{C}_{11}\text{H}_{14}\text{N}_2$ requires C, 75.85; H, 8.25; N, 16.15%); δ_{H} 7.75 (1H, d), 7.0-6.4 (5H, m), 7.90 (1H, d), 5.35 (1H, dd) and 2.80 (6H, s); m/z 174 (M^+ , 15%), 130 (11), 96 (23), 93 (35), 82 (100) and 77 (27); δ_{C} 161.18, 153.14 (q), 153.02, 128.61, 123.37, 120.44, 98.72 and 40.31: 1,1-diethyl-5-phenyl-1,5-diazapentadiene (94%), b.p. 156-159°C (0.1 Torr) (Found: C, 77.1; H, 8.75; N, 13.95. $\text{C}_{13}\text{H}_{18}\text{N}_2$ requires C, 77.2; H, 8.95, N, 13.85%); δ_{H} 7.95 (1H, d), 7.4-7.0 (5H, m), 6.75 (1H, d), 5.45 (1H, dd), 3.21 (4H, q) and 1.16 (6H, t); m/z 202 (M^+ , 53%), 173 (23), 157 (18), 145 (25), 130 (47), 110 (100), 104 (30) and 93 (22); δ_{C} 161.44, 153.06 (q), 151.03, 128.46, 123.04, 120.31, 97.76, 45.73 and 12.77: 1-ethyl-1-methyl-5-phenyl-1,5-diazapentadiene (92%), b.p. 130-133°C (0.1 Torr) (Found: C, 74.7; H, 8.55; N, 13.8. $\text{C}_{12}\text{H}_{16}\text{N}_2$ requires C, 76.55; H, 8.55; N, 14.90%);

δ_{H} 7.93 (1H, d), 7.4-7.0 (5H, m), 6.80 (1H, d), 5.39 (1H, dd), 3.21 (2H, q), 2.81 (3H, s) and 1.14 (3H, t); m/z 188 (M^+ , 48%), 159 (18), 96 (100), 93 (40) and 77 (52); δ_{C} 161.52, 152.88 (q), 128.42, 123.13, 120.26, 98.00, 49.32, 24.87 and 23.58: 1-iso-propyl-1-methyl-5-phenyl-1,5-diazapentadiene (50%), b.p. 171-173°C (0.1 Torr) (Found: C, 77.25; H, 8.95; N, 13.9.

$\text{C}_{13}\text{H}_{18}\text{N}_2$ requires C, 77.25; H, 8.9; N, 13.85%; δ_{H} 7.94 (1H, d), 7.4-7.0 (5H, m), 6.90 (1H, d), 5.40 (1H, dd), 3.52 (1H, septet), 2.73 (3H, s), 1.22 (3H, s) and 1.14 (3H, s); m/z 202 (M^+ , 39%), 159 (29), 130 (18), 110 (100) and 77 (32); δ_{C} 161.70, 153.33 (q), 151.21, 128.75, 123.43, 120.59, 98.47, 55.59, 31.82 and 20.44: 1,1,4-trimethyl-5-phenyl-1,5-diazapentadiene (91%), b.p. 104-106°C (0.1 Torr) (Found: C, 76.4; H, 8.6; N, 14.9.

$\text{C}_{12}\text{H}_{16}\text{N}_2$ requires C, 76.55; H, 8.55; N, 14.9%); ^1H n.m.r. showed two isomers to be present, the major isomer is reported first δ_{H} 7.3-6.6 (6H, m), 4.77, 5.18 (1H, d), 2.66, 2.83 (6H, s) and 2.20, 1.83 (3H, s); m/z 188 (M^+ , 44%), 173 (28), 144 (18), 96 (100) and 77 (34); (The minor isomer is recorded in brackets); δ_{C} 164.26 (165.09) (q), 152.13 (q), 148.07 (146.74), 128.31 (128.19), 121.61 (121.66), 120.55 (120.58), 92.33 (100.06), 40.11, 22.65 (16.16); 5-phenyl-1,1,3-trimethyl-1,5-diazapentadiene (74%), b.p. 132-136°C (0.1 Torr) (Found: C, 76.3; H, 8.4; N, 14.65. $\text{C}_{12}\text{H}_{16}\text{N}_2$ requires C, 76.55; H, 8.55; N, 14.88%); δ_{H} 7.72 (1H, s), 7.3-6.9 (5H, m), 6.28 (1H, s), 2.96 (6H, s) and 2.10 (3H, s); m/z 188 (M^+ , 44%), 173 (18), 159 (14), 144 (29), 96 (100) and 77 (86); δ_{C} 165.28, 153.75 (q), 152.26, 128.40, 122.89, 120.53, 105.84 (q), 42.57 and 10.68: 5-phenyl-1,1,2-trimethyl-1,5-diazapentadiene (64%), b.p. 127-130°C (0.1 Torr) (Found: C, 76.4; H, 8.6; N, 14.75. $\text{C}_{12}\text{H}_{16}\text{N}_2$ requires

C, 76.55; H, 8.55; N, 14.9%); δ_{H} 8.29 (1H, d), 7.3-7.0 (5H, m), 5.43 (1H, d), 2.90 (6H, s) and 2.10 (3H, s), m/z 188 (M^+ , 12%), 173 (9), 163 (6), 113 (100), 98 (23), 96 (35), 93 (35), 82 (11) and 77 (17); δ_{C} 159.58, 156.73 (q), 153.91(q), 128.68, 123.34, 120.59, 99.08, 39.63, 14.96.

1,5-diphenyl-2-methyl-1,5-diazapentadiene (86%), b.p. 140-144°C (0.1 Torr) (Found: C, 81.2; H, 6.55; N, 12.05.

$\text{C}_{16}\text{H}_{16}\text{N}_2$ requires C, 81.3; H, 6.8; N, 11.85%); δ_{H} 7.5-6.8 (11H, m), 5.02 (1H, d), 1.97 (3H, s); m/z 236 (M^+ , 100%), 235 (53), 221 (37), 145 (97), 118 (30), 93 (30) and 77 (53); δ_{C} 165.79 (q), 149.58 (q), 142.78 (q), 139.05, 129.24, 128.61, 122.87, 121.82, 121.14, 115.76, 97.65 and 20.79: 1,5-diphenyl-3-methyl-1,5-diazapentadiene (98%), m.p. 139-140°C (from ethanol) (Found: C, 81.4; H, 6.65; N, 12.1. $\text{C}_{12}\text{H}_{16}\text{N}_2$ requires C, 81.3; H, 6.8; N, 11.85%), δ_{H} 7.30 (2H, s), 7.2-6.6 (11H, m) and 1.85 (3H, s); m/z 236 (M^+ , 100%), 235 (76), 218 (22), 144 (27); 130 (17), 104 (17), 93 (12) and 77 (63). The ^{13}C n.m.r. spectrum was rather unusual in that it showed only five signals, δ_{C} 149.87 (br), 146.86 (q), 129.18, 122.92 and 117.73, with no signal for the methyl group and its quaternary. This did not change at all with temperature (0-52°C) and was also shown to be independent of field strength (20-90MHz). The peak for the central quaternary carbon could possibly overlap with the signals due to the phenyl ring. The broad peak at δ 149.87 may be due to a rapid exchange process involving the proton attached to the nitrogen. However, the apparent lack of signal from the methyl carbon is particularly strange, but could be caused by a particularly long relaxation time as, with a long pulse delay, a very broad peak centred at ca. δ 12.0 is observable.

1,5-Di-*o*-tolyl-1,5-diazapentadiene (80%), b.p. 127-132°C (0.2 Torr); δ_{H} 11.75 (1H, br s), 7.66 (2H, d), 7.3-6.9 (8H, m), 5.18 (1H, t) and 2.38 (6H, s) (^1H n.m.r. identical to literature spectrum¹⁶⁵); m/z 250 (M^+ , 100%), 144 (90), 107 (66) and 91 (29). 1,5-Di[$^2\text{H}_5$]phenyl-1,5-diazapentadiene (63%), m.p. 112-113°C; ^2H n.m.r. $\delta(\text{CHCl}_3)$ 7.22 (4 ^2H , s) and 6.98 (6 ^2H , s); m/z 232 (M^+ , 100%), 231 (49), 230 (95) and 82 (43).

[3- ^2H]-1,5-diphenyl-1,5-diazapentadiene.- The corresponding [3- ^1H] perchlorate (0.64g, 2mmol) was dissolved in [^2H] trifluoroacetic acid (5ml). This solution was neutralised with a solution of sodium deuterioxide and was extracted three times with ether. The organic extracts were dried (Na_2SO_4) and concentrated to give the [3- ^2H] base (0.18g, 43%); ^1H n.m.r. showed a broad singlet at δ 8.27 and no peaks at $\delta < 6$; m/z 223 (M^+ , 100%), 222 (95); there was no significant peak corresponding to [$^2\text{H}_2$] species.

PYROLYSIS OF 1,5-DIAZAPENTADIENES

(i) Pyrolysis of 1,1-Dialkyl-5-phenyl-1,5-diazapentadienes

(a) 1,1-Dimethyl-5-phenyl-1,5-diazapentadiene. 0.108g (0.62 mmol), 100°C, 800°C, 2×10^{-3} Torr, 180min: 1-methylpyrrole (44%), m/z 81 (M^+ , 100%), 80 (54) and 42 (60); aniline (30%), m/z 93 (M^+ , 100%), 66 (85) and 65 (92); quinoline (10%), m/z 129 (M^+ , 100%), 102 (40) and 51 (30); residue in inlet-3%. The pyrolysis was then repeated on a larger scale and, using preparative g.c. (10% carbowax) the products were separated

out and their identity confirmed by ^1H n.m.r. spectroscopy: 1-methylpyrrole δ_{H} 6.58 (2H, t), 6.13 (2H, t) and 3.63 (3H, s); aniline δ_{H} 7.2-6.3 (5H, m) and 3.35 (2H, br s); quinoline δ_{H} 8.90 (1H, d) and 8.2-7.2 (6H, m).

(b) 1,1-Diethyl-5-phenyl-1,5-diazapentadiene. 0.097g (0.48mmol), 140°C, 800°C, 7×10^{-3} Torr, 60 min: aniline (41%), m/z 93 (M^+ , 100%), 66 (50) and 65 (23); 1-ethylpyrrole (24%), m/z 95 (M^+ , 75%), 80 (100) and 41 (46); 1-ethyl-2-methylpyrrole (13%), m/z 109 (M^+ , 100%), 94 (61) and 80 (88); *N*-methylaniline (13%), 107 (M^+ , 83%), 106 (100) and 77 (42); quinoline (5%), m/z 129 (100), 102 (32) and 51 (27), residue in inlet - nil. The pyrolysis was then repeated on a larger scale and using preparative g.c. (10% carbowax) the products were separated out and their ^1H n.m.r. spectra recorded: aniline δ_{H} 7.2-6.5 (5H, m) and 3.45 (2H, br s); 1-ethylpyrrole δ_{H} 6.67 (2H, t), 6.13 (2H, t), 3.92 (2H, q) and 1.42 (3H, t); 1-ethyl-2-methylpyrrole δ_{H} 6.57 (2H, t), 6.03 (1H, t), 5.84 (1H, m), 3.83 (2H, q), 2.21 (3H, s), and 1.34 (3H, t); *N*-methylaniline δ_{H} 7.1-6.5 (5H, m), 3.50 (1H, br s) and 2.72 (3H, s); quinoline δ_{H} 8.88 (1H, d) and 8.2-7.2 (6H, m).

(c) 1-Ethyl-1-methyl-5-phenyl-1,5-diazapentadiene. 0.109g (0.58mmol), 140°C, 800°C, 4×10^{-3} Torr, 60 min: aniline (37%), m/z 93 (M^+ , 100%), 66 (30) and 65 (18); 1-methylpyrrole (21%), m/z 81 (M^+ , 100%), 80 (69) and 53 (32); 1,2-dimethylpyrrole (14%), m/z 95 (M^+ , 73%), 94 (100) and 53 (15); 1-ethylpyrrole (13%), m/z 95 (M^+ , 75%), 80 (100) and 41 (23); *N*-methylaniline (7%), m/z 107 (M^+ , 80%), 106 (100) and 77 (33); quinoline (8%), m/z 129 (M^+ , 100%), 102 (24) and 103 (17); residue in inlet - 3%.

(d) 1-Isopropyl-1-methyl-5-phenyl-1,5-diazapentadiene.

0.038g, (0.19mmol), 140-160°C, 800°C, $3-5 \times 10^{-3}$ Torr, 40 min: aniline (23%), m/z 93 (M^+ , 100%), 66 (32) and 65 (18); 1,2-dimethylpyrrole (21%), m/z 95 (M^+ , 67%), 94 (100) and 53 (15); *N*-methylaniline (14%), m/z 107 (M^+ , 91%), 106 (100) and 77 (36); pyrrole (8%), m/z 67 (M^+ , 100%), 66 (8) and 41 (53); 1-isopropylpyrrole (6%), m/z 109 (M^+ , 26), 95 (29) and 94 (100); quinoline (5%) m/z 129 (M^+ , 100%), 102 (28) and 76 (12); residue in inlet - 5%.

(e) 5-Phenyl-1,1,4-trimethyl-1,5-diazapentadiene. 0.134g

(0.71mmol), 100°C, 800°C, 4×10^{-3} Torr, 60min: 2-methylquinoline (43%), m/z 143 (M^+ , 100%), 115 (20), 128 (16); 1,3-dimethylpyrrole (20%), m/z 95 (M^+ , 64%), 94 (100) and 53 (16). Although there was no authentic sample for comparison by g.c., the 1H n.m.r. spectrum of the crude pyrolysate showed signals identical to those of the 1,3-dimethylpyrrole isolated in (f) below; aniline (19%), m/z 93 (M^+ , 100%), 66 (33) and 65 (19); residue in inlet - 1%. The pyrolysis was then repeated on a larger scale and, using preparative g.c. (10% carbowax) it was attempted to separate out the products. However 1,3-dimethylpyrrole was not isolated. Those products which were isolated had their identity confirmed by 1H n.m.r. spectroscopy: aniline δ_H 7.2-6.5 (5H, m) and 3.55 (2H, br s); 2-methylquinoline δ_H 8.03 (1H, m), 7.94 (1H, m), 7.8-7.2 (4H, m) and 2.70 (3H, s).

(f) 5-Phenyl-1,1,3-trimethyl-1,5-diazapentadiene. 0.076g

(0.41mmol), 120°C, 800°C, 3×10^{-3} Torr, 60 min: aniline (44%), m/z 93 (M^+ , 100%), 66 (31) and 65 (18); 1,3-dimethylpyrrole (49%), m/z 95 (M^+ , 62%), 94 (100) and 42 (15); 3-methylquinoline

(25%), m/z 143 (M^+ , 100%), 115 (39) and 89 (14); quinoline (21%), m/z 129 (M^+ , 100%), 102 (25) and 76 (13); *N*-methylaniline (13%), m/z 107 (M^+ , 100%), 106 (80) and 77 (39); residue in inlet - 1%. The pyrolysis was then repeated on a larger scale and, using preparative g.c. (10% carbowax) the products were separated out and their identity was confirmed by ^1H n.m.r. spectroscopy: aniline δ_{H} 7.2-6.5 (5H, m) and 3.50 (2H, br s); *N*-methylaniline δ_{H} 7.2-6.5 (5H, m), 3.50 (1H, br s) and 2.78 (3H, s); 1,3-dimethylpyrrole δ_{H} 6.46 (1H, t), 6.35 (1H, br s), 5.93 (1H, m), 3.54 (3H, s) and 2.05 (3H, s); quinoline δ_{H} 8.90 (1H, dd), 8.16 (1H, t), 8.08 (1H, m) and 7.8-7.3 (4H, m); 3-methylquinoline δ_{H} 8.75 (1H, d), 8.2-7.3 (5H, m) and 2.52 (3H, s).

(g) 5-Phenyl-1,1,2-trimethyl-1,5-diazapentadiene. 0.116g (0.62mmol), 160°C, 800°C, 5×10^{-3} Torr, 45 min: aniline (33%), m/z 93 (M^+ , 100%), 66 (43) and 65 (25); 4-methylquinoline (26%), m/z 143 (M^+ , 100%), 115 (33) and 89 (11); 1,2-dimethylpyrrole (10%), m/z 95 (M^+ , 67%), 94 (100) and 53 (15); *N*-methylaniline (trace), m/z 107 (M^+ , 92%), 106 (100) and 77 (20); residue in inlet - 3%. The pyrolysis was then repeated on a larger scale and, using preparative g.c. (10% carbowax) the products were separated out and their identity was confirmed by ^1H n.m.r. spectroscopy: aniline δ_{H} 7.2-6.5 (5H, m) and 2.75 (2H, br s); 4-methylquinoline δ_{H} 8.73 (1H, d), 8.2-7.1 (5H, m) and 2.63 (3H, s); 1,2-dimethylpyrrole δ_{H} 6.48 (1H, t), 5.99 (1H, t), 5.84 (1H, m), 3.47 (3H, s) and 2.17 (3H, s); *N*-methylaniline δ_{H} 7.2-6.5 (5H, m) and 2.78 (3H, s).

(ii) Pyrolysis of 1,5-Diaryl-1,5-diazapentadienes

- (a) 1,5-Diphenyl-1,5-diazapentadiene¹⁶⁶ 0.055g (0.25mmol), 100°C, 800°C, 3×10^{-3} Torr, 45 min: aniline (33%), m/z 93 (M^+ , 100%), 66 (49) and 65 (17); quinoline (20%), m/z 129 (M^+ , 100%), 103 (19) and 102 (28); residue in inlet - 17%.
- (b) 1,5-Diphenyl-2-methyl-1,5-diazapentadiene. 0.082g, (0.35mmol), 140-180°C, 800°C, 5×10^{-3} Torr, 45 min: aniline (56%), m/z 93 (M^+ , 100%), 66 (32) and 65 (18); *N*-methylaniline (trace), m/z 107 (M^+ , 83%), 106 (100) and 93 (86); 2-methylquinoline (54%), m/z 143 (M^+ , 100%), 129 (72) and 128 (33); 4-methylquinoline (12%), m/z 143 (M^+ , 100%), 115 (33) and 89 (11); residue in inlet - 3%. The quinolines were identified by g.c. comparison with authentic samples: the presence of 4-methylquinoline was confirmed by "spiking" the n.m.r. solution with the authentic sample.
- (c) 1,5-Diphenyl-3-methyl-1,5-diazapentadiene. 0.099g (0.42mmol), 140°C, 800°C, 4×10^{-3} Torr, 45 min: aniline (49%), m/z 93 (M^+ , 100%), 66 (30) and 65 (17); *N*-methylaniline (19%), m/z 107 (M^+ , 85%), 106 (100) and 93 (81); quinoline (55%), m/z 129 (M^+ , 100%), 102 (25) and 76 (12); 3-methylquinoline (4%), m/z 143 (M^+ , 100%), 115 (38) and 89 (12); residue in inlet - 4%. The minor and major quinolines were identified as above.
- (d) 1,5-Di-*o*-tolyl-1,5-diazapentadiene. 0.085g (0.34mmol) 120-130°C, 800°C, 4×10^{-3} Torr, 45 min: aniline (trace) m/z 93 (M^+ , 100%), 66 (35) and 65 (20); *o*-toluidine (40%), m/z 107 (M^+ , 98%), 106 (100) and 77 (20); quinoline (trace),

m/z 129 (M^+ , 100%), 102 (36) and 76 (18); 8-methylquinoline (40%), m/z 143 (M^+ , 100%), 116 (16) and 115 (31); 4-methylquinoline (4%), m/z 143 (M^+ , 100%), 142 (51) and 115 (23); recovered starting material (12%); indole (trace), m/z 117 (M^+ , 100%), 90 (44) and 89 (25); residue in inlet 5%. 1H n.m.r. "spiking" experiments using authentic samples definitely showed that 3-methylquinoline was absent and 4-methylquinoline was present. The base was then pyrolysed on a preparative scale (3.70g, 14.8mmol) at 850°C and 3×10^{-3} Torr (inlet temperature 150°C) over a period of 3h to give a liquid pyrolysate of 2.65g (residue in inlet - 20%).

8-Methylquinoline was isolated by the Hinsberg method.¹⁶⁷ The liquid pyrolysate was suspended in a solution of sodium hydroxide (2-3g) in water (50ml) and *p*-toluenesulphonyl chloride (6.0g, *ca.* 2 x excess) was added. The mixture was stirred at room temperature for 3h and was then steam distilled. The distillate was saturated with sodium chloride, extracted with methylene chloride (3x30ml) and the organic extracts were dried (Na_2SO_4) and concentrated. The residue was purified by bulb-to-bulb distillation at reduced pressure to give a mixture of the quinolines (0.99g) from which pure 8-methylquinoline picrate was obtained by recrystallisation of the mixed picrate salts from ethanol. The picrate had m.p. 199-201°C (lit.,¹⁶⁸ 200°C), δ_H (200MHz, [2H_6]D.M.S.O.) 9.19 (1H, dd), 9.12 (1H, dd), 8.51 (2H, s), 8.14 (1H, d), 8.05 (1H, dd), 7.93 (1H, br d), 7.78 (1H, t) and 2.77 (3H, s).

(e) 1,5-Di(2H_5)phenyl)-1,5-diazapentadiene. 0.062g (0.27mmol), 100°C, 800°C, 3×10^{-3} Torr, 45 min, residue in inlet - 7%.

The entire pyrolysate was dissolved in [^2H]chloroform and analysed by ^1H n.m.r. at 360MHz, which showed significant peaks at 8.92 (1.0H, m), 8.15 (1.01H, m) and 7.39 (0.53H, dd), due to the 2-, 4- and 3-protons of quinoline respectively. Deuterium incorporation at position 3 is 47%.

(f) [3- ^2H]-1,5-Diphenyl-1,5-diazapentadiene. 0.071g, (0.32 mmol), 100°C, 800°C, 4×10^{-3} Torr, 60 min, residue in inlet - 7%. The ^1H n.m.r. spectrum (360MHz) showed signals at δ 9.19 (1.0H, complex) and δ 8.70 (1.0H, complex) due to H(2) and H(4) respectively, with both showing partial coupling to H(3). The ^1H at position 3 gave a double doublet which overlapped with a doublet of triplets at δ 7.80 (1.44H); the chemical shift was confirmed by ^2H n.m.r. $\delta(\text{CHCl}_3)$ 7.83. This chemical shift is different to that found in previous examples *e.g.* (e), but variation of chemical shift with concentration is well known in quinolines. Protium incorporation at position 3 is therefore 44%.

Copyrolysis of 1,5-di-*p*-tolyl-1,5-diazapentadiene and 1,5-diphenyl-3-methyl-1,5-diazapentadiene (for method, see ref.64), di-*p*-tolyl derivative (0.033g, 0.13mmol), diphenyl derivative (0.034g, 0.14mmol), 150°C, 850°C, 3×10^{-3} Torr, 45 min. Residues in inlet 22% and 4% respectively. Analysis by g.l.c. (5% Carbowax, 140°C) showed the presence of *N*-methylaniline m/z 107 (M^+ , 91%), 106 (100) and 77 (31); aniline m/z 93 (M^+ , 100%), 66 (32) and 65 (18); *N*-methyl-*p*-toluidine m/z 121 (M^+ , 83%), 120 (100) and 106 (40); and *p*-toluidine m/z 107 (M^+ , 86%), 106 (100) and 77 (15). Assignments were confirmed

by comparison with authentic samples and by g.c./m.s.

Copyrolysis of *N*-methylaniline and *p*-toluidine. *N*-Methylaniline (0.220g, 2.05mmol), *p*-toluidine (0.210g, 1.95mmol), 80-100°C, 850°C, 5×10^{-3} Torr, 60 min. Only starting materials were detected by g.l.c. (5% Carbowax, 130°C).

Pyrolysis of 1-isopropylpyrrole. 0.28g, (2.57mmol), 25°C, 800°C, 3×10^{-3} Torr, 90 min: It was found by ^1H n.m.r. that the pyrolysate consisted of a mixture of 1-isopropylpyrrole and pyrrole in a 1:3 ratio.

Preparation of Authentic Samples for Comparison with Pyrolysates

2-Methylpyrrole.⁻¹²⁷ Pyrrole-2-aldehyde (5g, 0.05mol) was added at room temperature to a mixture of potassium hydroxide (10g, 0.18mol) (crushed pellets), hydrazine hydrate (90%, 7.5 ml) and diethylene glycol (100ml), from which water (2-3ml) had been distilled. The mixture was heated under reflux for 15 min before it was slowly distilled through a short vigreux column to give 2-methylpyrrole (mixed with some water, hydrazine and glycol) (b.p. 96-104°C). The total distillate was placed in a micro separating funnel and the upper layer (2-methylpyrrole) was separated off (3.25g, 76%) δ_{H} 6.47 (1H, m), 6.08 (1H, m), 5.85 (1H, br m) and 2.14 (3H, s). The product was shown by ^1H n.m.r. spectroscopy to be pure enough for use without further distillation.

Preparation of 1-Alkylpyrroles.⁻¹²⁸ Dry dimethyl sulphoxide (100ml) was added to potassium hydroxide (11.2g, 0.2mol) (crushed pellets) and the mixture was stirred for 5 min.

The appropriate pyrrole (0.05mol) was then added and the mixture was stirred for 45 min. The mixture was cooled briefly and the appropriate alkyl halide (0.1mol) was added before the mixture was stirred for a further 45 min. Water (100ml) was added and the mixture was extracted with ether (3x50ml), and the extracts were washed with water (3x25ml). The combined extracts were dried (Na_2SO_4) and the solvent and excess of alkyl halide were removed *in vacuo* (10 Torr) at low temperature. The crude product was then purified by bulb-to-bulb distillation at atmospheric pressure and with the receiver bulb cooled by solid carbon dioxide. These conditions may explain discrepancies with literature boiling points. The following compounds were prepared by this general procedure:

1-ethylpyrrole (65%) b.p. 126-130°C (lit.¹⁶⁹ b.p. 127-130°C) δ_{H} 6.55 (2H, m), 6.14 (2H, m), 3.92 (2H, q) and 1.41 (3H, t):

1-ethyl-2-methylpyrrole (72%) b.p. 135-137°C (lit.¹⁷⁰ b.p. 157°C). δ_{H} 6.56 (1H, m), 6.04 (1H, m), 5.85 (1H, br m), 4.83 (2H, q), 2.20 (3H, s) and 1.35 (3H, t):

1,2-dimethylpyrrole (74%) b.p. 102-104°C (lit.¹⁷¹ b.p. 139-140°C) δ_{H} 6.51 (1H, t), 5.99 (1H, t), 5.86 (1H, br m), 3.47 (3H, s) and 2.18 (3H, s):

1-isopropylpyrrole (68%) b.p. 135-138°C (lit.¹⁷² b.p. 49-51°C/21 Torr) δ_{H} 6.80 (2H, m), 6.22 (2H, m), 2.46 (1H, septet), 1.55 (3H, s) and 1.47 (3H, s).

PART 2PREPARATION AND PYROLYSIS OF HETERO-2-AZADIENESPreparation of 1,4-Diphenyl-1,2-diazabutadiene

(a) α -Chloro-t-butyl acetoacetate.- t-Butyl acetoacetate (17g, 108mmol) was suspended in dry chloroform (50ml) and the solution was heated to reflux. Sulphuryl chloride (13.4g, 108mmol) was then added dropwise and the mixture was heated under reflux for a further 1h. The solvent was removed under vacuum and the residual liquid was distilled to give a colourless liquid (13.72g, 66%) b.p. 98°C (10 Torr) [lit.¹⁷³ 92°C (18 Torr)].

(b) t-Butyl-1-chloropyruvate phenylhydrazone.- A solution of sodium nitrite (1.8g, 22.6mmol) in water (3ml) was slowly added to a solution of aniline (2.1g, 22.6mmol) in 15% aqueous hydrochloric acid (10ml). The diazotization was conducted at 0-5°C and was complete after the mixture had been stirred for 5 min. Sodium bicarbonate was then added to decrease the acidity of the solution to pH=5-6. α -Chloro-t-butylacetoacetate (4.3g, 22.6mmol) suspended in cold methanol (30ml) was slowly added followed by sodium acetate (1.7g). The mixture was stirred overnight at 5°C and the yellow precipitate which formed was filtered off and washed with water to give the hydrazone which was dried *in vacuo* over phosphorus pentoxide (4.27g, 75%), m.p. 84°C (lit.¹⁷³ 88°C).

(c) Formyltriphenylphosphonium phenylhydrazone perchlorate.-

A mixture of triphenylphosphine (2.52g, 0.01mol) and t-butyl 1-chloropyruvate phenylhydrazone (2.54g, 0.01mol) was heated at 140-160°C (oil bath) until gas evolution (isobutene and carbon dioxide) ceased (15-20 min). The cooled solid product was dissolved in ethanol (with heating) and the solution was treated with 65% aqueous perchloric acid (1.1ml). The precipitate which formed was filtered and washed with cold ethanol to give the required product (4.56g, 94%) m.p. 182-183°C (lit.¹⁷⁴ 180°C).

(d) 1,4-Diphenyl-1,2-diazabutadiene.- A mixture of formyltriphenylphosphonium phenylhydrazone perchlorate (4.3g, 9mmol), benzaldehyde (0.95g, 9mmol) and triethylamine (1.1g, 11mmol) in 1,1-dichloroethane (45ml) was heated under reflux for 2h. The solvent was removed under vacuum and the residual oil was triturated with toluene. The brown solid which formed was filtered to remove triethylammonium perchlorate and the filtrate was concentrated under reduced pressure. Chromatography of the residue on silica gel (with methylene chloride as eluent) gave the required compound as an orange/red solid (0.38g, 20%) m.p. 113-115°C (lit.¹⁷⁴ 111°C) δ_{H} 8.1-7.1 (12H, m); m/z 208 (M^+ , 15%), 207 (14), 103 (21) and 77 (100).

Preparation of 1-(o-chlorophenyl)-4-phenyl-1,2-diazabutadiene.

The method of preparation was the same as that used for 1,4-diphenyl-1,2-diazabutadiene, except that o-chloroaniline was used in part (b) instead of aniline.

(b) t-Butyl-1-chloropyruvate o-chlorophenylhydrazine, (55%)
m.p. 57-59°C; this compound was reported in ref. 174 but no
melting point was given so its purity was checked by ^1H n.m.r.;
 δ_{H} 8.73 (1H, s), 7.6-6.8 (4H, m) and 1.59 (9H, s).

(c) Formyltriphenylphosphonium o-chlorophenylhydrazone
perchlorate, (73%) m.p. 120-121°C (lit.,¹⁷⁴ 127°C).

(d) 1-(o-Chlorophenyl)-4-phenyl-1,2-diazabutadiene¹⁷⁴ (7%).
A semi solid was obtained which decomposed when distilled, but
was identified by n.m.r. and mass spectroscopy; δ_{H} 8.1-7.0
(11H, m); m/z 244 (M^+ , 19%), 243 (23), 242 (73), 241 (69),
111 (50), 102 (100) and 77 (73).

1-Phenyl-4-(p-chlorophenyl)-1,2-diazabutadiene. - The method
of preparation was the same as that used for 1,4-diphenyl-1,2-
diazabutadiene, except that p-chlorobenzaldehyde was used in
part (d) instead of benzaldehyde. (29%) m.p. 102-104°C (Found:
C, 69.15; H, 4.6; N, 11.55. $\text{C}_{14}\text{H}_{11}\text{N}_2$ requires C, 69.3;
H, 4.55; N, 11.55%); δ_{H} 8.1-7.3 (11H, m) m/z 244 (M^+ ^{37}Cl ,
28%), 242 (M^+ ^{35}Cl , 78%), 207 (55), 178 (8), 137 (70), 101 (50)
and 77 (100); δ_{C} 152.78 (q), 146.70, 140.68, 135.35 (q),
133.36 (q), 130.78, 129.09, 128.94 (2C) and 122.59.

Preparation of Benzylidene Aniline and Substituted Analogues. -

The appropriately substituted aniline (20 mmol) was added to
a solution of the appropriately substituted benzaldehyde (20
mmol) in light petroleum (40/60) (5 ml). The exothermic reaction
produced a yellow liquid which crystallised as it cooled. The

crystals were then filtered off and washed with light petroleum (40/60). The following compounds were prepared in this way: benzylidene aniline (80%) m.p. 47-50°C (from ethanol) (lit.,¹⁷⁵ 51°C); δ_{H} 8.22 (1H, s), 7.9-7.7 (2H, m) and 7.4-7.0 (8H, m); m/z 181 (M^+ , 64%), 104 (18), 78 (20) and 77 (100): *p*-chloro-benzylidene aniline (95%) m.p. 61-63°C (from ethanol) (lit.,¹⁷⁶ 62°C); δ_{H} 8.34 (1H, s), 7.8-7.7 (2H, m) and 7.4-7.1 (7H, m); m/z 217 (M^+ ^{37}Cl , 19%), 215 (M^+ ^{35}Cl , 56), 104 (15) and 77 (100): benzylidene *o*-chloroaniline (21%) m.p. 50-52°C (from ethanol) (lit.,¹⁷⁷ 54°C); δ_{H} 8.27 (1H, s), 7.9-7.7 (2H, m) and 7.5-6.9 (7H, m); m/z 217 (M^+ ^{37}Cl , 33%), 215 (M^+ ^{35}Cl , 100%), 180 (18), 152 (14), 111 (60), 78 (26) and 77 (48).

Pyrolysis of 1,2-Diazabutadienes

(a) 1,4-Diphenyl-1,2-diazabutadiene, 0.031 g (0.15 mmol), 120-140°C, 650°C, 1×10^{-3} Torr, 30 min: benzylidene aniline (59%) m/z 181 (M^+ , 72%), 78 (21) and 77 (100). Residue in inlet - nil.

^1H N.m.r. spectroscopy and g.c. showed benzylidene aniline to be the only product in the pyrolysate; δ_{H} 8.44 (1H, s), 7.9-7.8 (2H, m) and 7.5-7.1 (8H, m). The crude, solid pyrolysate was scraped out of the trap and identified by its melting point 46-49°C and mixed melting point (with authentic) 47-50°C (lit.,¹⁷⁵ 51°C).

(b) 1-Phenyl-4-(*p*-chlorophenyl)-1,2-diazabutadiene. - The vertical furnace f.v.p. apparatus was used here due to some

decomposition of the starting material at 160°C, in the inlet to the horizontal furnace - 0.109g, 0.45mmol, 650°C, 7×10^{-3} Torr: *p*-chlorobenzylidene aniline (48%) m/z 217 (M^+ ^{37}Cl , 3%), 215 (M^+ ^{35}Cl , 44%), 104 (14) and 77 (100).

(c) 1-(*o*-Chlorophenyl) - 4 - phenyl-1,2-diazabutadiene.- The vertical furnace f.v.p. apparatus was used here due to complete decomposition of the starting material at 140°C, in the inlet to the horizontal furnace - 0.062g, 0.26mmol, 650°C, 4.5×10^{-3} Torr: Benzylidene *o*-chloroaniline (14%) m/z 217 (M^+ ^{37}Cl , 35%), 215 (M^+ ^{35}Cl , 100%), 111 (42) and 77 (52).

Preparation of Alkyl 3-(Phenylazo)but-2-enoates

(a) Preparation of Alkylchloroacetoacetate.- Alkyl acetoacetate (0.4mol) was stirred and cooled to 0°C and sulphuryl chloride (0.4mol) was added dropwise. The reaction, which began immediately with the evolution of sulphur dioxide and hydrogen chloride, was completed by warming on a water bath for 15 min. The crude product was diluted with ether (200ml) and the ethereal solution was repeatedly washed with small amounts of water until free from acid. The organic solution was dried (Na_2SO_4) and the ether was removed *in vacuo* leaving a colourless liquid. The following compounds were prepared using this method: ethyl chloroacetoacetate, (87%), [b.p. 110-112°C (30-35Torr)] [lit.¹⁷⁸ 105-110°C (30Torr)]; methyl chloroacetoacetate, (84%) [b.p. 92-95°C (10Torr)] (lit.¹⁷⁹ 137°C).

(b) Preparation of Alkyl 3-(phenylazo)but-2-enoates.-

Phenylhydrazine (0.1mol) was dissolved in dry ether (150ml) and a solution of the appropriate alkyl chloroacetoacetate (0.05mol) in dry ether (75ml) was added dropwise over 1h and then stirred for a further 1h. The mixture was filtered to remove the phenylhydrazine hydrochloride which had formed and the solvent was removed *in vacuo* from the red ether solution. The following compounds were prepared using this method:

methyl 3-(phenylazo)but-2-enoate (52%). A red oil was formed, which slowly solidified over a long period of time; b.p. 88-92°C (0.1Torr) (bulb-to-bulb distillation), (lit.¹⁸⁰ m.p. 46°C); δ_{H} 7.85-7.3 (5H, m), 6.78 (1H, q), 3.78 (3H, s) and 2.33 (3H, d); m/z 204 (M^+ , 26%), 173 (8), 105 (44) and 77 (100); ethyl 3-(phenylazo)but-2-enoate (73%) m.p. 49-50°C (from methanol) (lit.¹⁸⁰ 51°C); δ_{H} 7.9-7.8 (2H, m), 7.5-7.4 (3H, m), 6.78 (1H, q), 4.28 (2H, q), 2.41 (3H, d) and 1.34 (2H, t); m/z 218 (M^+ , 25%), 173 (8), 105 (45) and 77 (100).

Pyrolysis of Alkyl 3-(phenylazo)but-2-enoates

(a) Methyl 3-(phenylazo)but-2-enoate.- 0.163g (0.80mmol), 80-100°C, 650°C, 5×10^{-3} Torr, 60 min: The g.c. trace showed two peaks and g.c./m.s. identified the first peak as aniline m/z 93 (M^+ , 100%), 66 (44) and 65 (25). The second peak was tentatively identified as methyl glyoxylate anil m/z 163 (M^+ , 20%), 104 (93) and 77 (100). Several attempts were made to prepare an authentic sample of this compound, but were unsuccessful. Amongst the reactions tried was a Wittig

reaction of methyl (triphenylphosphoranylidene)acetate with nitrosobenzene, and the Wadsworth-Emmons modification of the Wittig reaction of the appropriate phosphonate⁴⁵ with nitrosobenzene using either potassium hydroxide or sodium hydride as the base.

(b) Ethyl-3-(phenylazo)but-2-enoate.- 0.130g (0.60mmol), 100°C, 650°C, 5×10^{-3} Torr, 45 min: The g.c. trace showed five peaks and t.l.c. showed six spots. Aniline was identified by g.c./m.s. m/z 93 (M^+ , 100%), 66 (50) and 65 (24).

Preparation of 3-Dimethylamino-2-azaprop-2-en-1-ones.¹⁷¹ The appropriate amide (0.05mol) was mixed with *N,N*-dimethylformamide diethylacetal (0.075mol) and dioxan (10g), and was heated at 80°C for 2h. The ethanol formed during the course of the reaction and the dioxan was removed *in vacuo* and the product was purified either by distillation or recrystallisation. The following compounds were made by this method.

3-Dimethylamino-1-methyl-2-azaprop-2-en-1-one, (91%) (from acetamide), b.p. 71°C (0.4Torr) (lit.¹⁷¹ 60°C (0.25Torr)); ν_{\max} 1650 cm^{-1} (CO); ^1H n.m.r. showed two isomers to be present, the major isomer is reported first δ_{H} 8.09, 7.25 (1H, s), 2.86, 2.69 (3H, s), 2.79, 2.59 (3H, s) and 1.87, 1.69 (3H, s); m/z 114 (M^+ , 41%), 99 (100) and 43 (33); δ_{C} 184.06 (q), 159.40, 40.76, 23.59 and 26.46: 3-dimethylamino-1-ethyl-2-azaprop-2-en-1-one, (81%) (from propionamide), b.p. 76-78°C (0.1 Torr) (Found: C, 52.7; H, 9.6; N, 20.35. $\text{C}_6\text{H}_{12}\text{N}_2\text{O}\frac{1}{2}\text{H}_2\text{O}$ requires, C, 52.55; H, 9.5; N, 20.45%); ν_{\max} 1650 cm^{-1} (CO); ^1H n.m.r. showed two isomers to be present, the major isomer is reported first δ_{H} 8.37, 7.98 (1H, br s), 3.07, 2.92 (3H, s),

3.02, 2.84 (3H, s), 2.43, 2.23 (2H, q) and 1.10, 1.11 (3H, t); m/z 128 (M^+ , 3%), 99 (73), 73 (95) and 44 (100): δ_c 187.65 (q), 159.68, 40.81, 34.66, 32.68 and 9.31:

3-dimethylamino-1-phenyl-2-azaprop-2-en-1-one (93%) from benzamide m.p. 75-76°C (from ether) (lit.¹⁷¹ 67-69°C); ν_{\max} 1650 cm^{-1} (CO); δ_H 8.42 (1H, s), 8.2-8.1 (2H, m), 7.35-7.15 (3H, m), 2.91 (3H, s) and 2.83 (3H, s); m/z 176 (M^+ , 58%), 105 (81), 99 (100) and 77 (84); δ_c 177.43 (q), 160.44, 136.62 (q), 131.55, 129.49, 127.66, 41.02 and 34.97.

Preparation of 3-Dimethylamino-1-phenyl-2-azaprop-2-en-1-thione¹⁷¹.

A mixture of thiobenzamide (10g, 0.07mol) and *N,N*-dimethylformamide diethylacetal (35g, 0.23mol) was heated for 1h at 50°C. The ethanol formed during the course of the reaction was then removed *in vacuo* and the solid formed was filtered off and washed with ether to give a red solid (8.65g, 62%), m.p. 57-59°C (lit.¹⁷¹ 50-54°C); ν_{\max} 965 cm^{-1} (CS); δ_H 8.73 (1H, s), 8.5-8.35 (2H, m), 7.5-7.25 (3H, m) and 3.23 (6H, s); m/z 192 (M^+ , 39%), 159 (43), 121 (100) and 115 (39); δ_c 215.48 (q), 158.73, 142.79 (q), 131.46, 128.50, 127.29, 41.49 and 35.98.

Attempted Preparation of 3-Dimethylamino-2-azaprop-2-en-1-one.

A mixture of formamide (4.5g, 0.1mol) and *N,N*-dimethylformamide diethylacetal in dioxan (20g) was heated at 80°C for 2h, and during this time changed from pale yellow to dark brown. The mixture was shown by ^1H n.m.r. spectroscopy, g.c. and g.c./m.s. to consist only of dimethylformamide and ethanol in dioxan.

Attempted Preparation of 3-Dimethylamino-1-methyl-2-azaprop-2-en-1-thione.

A mixture of thioacetamide (3.75g, 25mmol) and *N,N*-dimethylformamide diethylacetal (7.35g, 25mmol) was heated for 1h at 50°C. The ethanol which was formed during the course of the reaction was removed *in vacuo* before the remaining semi solid was triturated with ether. The crystals which formed were filtered off, washed with cyclohexane and were dried to give a brown solid (2.04g) m.p.150°C (from ethanol) δ_{H} 8.82 (1H, s), 8.19 (1H, d), 5.88 (1H, d), 3.11 (6H, s) and 3.08 (6H, s); m/z 185 (M^+ , 96%), 152 (17), 130 (100), 114 (30), 97 (30) and 82 (30). The ^1H n.m.r. spectrum and m.s. suggest that the compound formed is *N*-(3-aminothioacryloyl)-formamidine. This compound has subsequently been prepared by Liebscher¹³⁷ using a similar method.

Another attempt to prepare the title compound involved the use of Lawesson's reagent¹⁸² for the thiation of 3-dimethylamino-1-methyl-2-azaprop-2-en-1-one. However this was also unsuccessful.

Pyrolysis of 3-Dimethylamino-2-azaprop-2-en-1-ones (or thiones).

(a) 3-Dimethylamino-1-methyl-2-azaprop-2-en-1-one 0.152g (1.33mmol), 70°C, 900°C, 5×10^{-3} Torr, 60 min: *N,N*-dimethylformamide (29%) m/z 73 (M^+ , 100%), 72 (8) and 58 (8); acetonitrile (24%). This was clearly shown to be present by ^1H n.m.r. spectroscopy and by g.c. comparison with an authentic sample. However, under g.c./m.s. conditions the peak was too close to the solvent for resolution; dimethylacetamide (trace)

m/z 87 (M^+ , 34%), 72 (10) and 44 (100); *N,N*-dimethylcyanamide (trace) was tentatively identified due to the presence of the correct molecular ion in the g.c./m.s., m/z 70 (M^+ , 37%), 69 (72) and 42 (100). Residue in inlet - 7%.

(b) 3-Dimethylamino-1-ethyl-2-azaprop-2-en-1-one. 0.173g (1.35mmol), 80°C, 900°C, 5×10^{-3} Torr, 30 min: *N,N*-dimethylformamide (16%) m/z 73 (M^+ , 56%), 72 (5) and 44 (100); propionitrile (27%). This was not detected by g.c./m.s. due to overlap with the solvent peak, but was clearly shown to be present by 1H n.m.r. spectroscopy. Residue in inlet - 5%.

(c) 3-Dimethylamino-1-phenyl-2-azaprop-2-en-1-one. 0.085g (0.483mmol), 140°C, 900°C, 5×10^{-3} Torr, 60 min: *N,N*-dimethylformamide (30%) m/z 73 (M^+ , 53%) and 40 (100); benzonitrile (35%) m/z 103 (M^+ , 100%), 76 (49) and 75 (11); residue in inlet - 5%.

(d) 3-Dimethylamino-1-phenyl-2-azaprop-2-en-1-thione. 0.175g (0.91mmol), 140-160°C, 900°C, 3×10^{-3} Torr, 45 min: *N,N*-dimethylthioformamide (35%) m/z 89 (M^+ , 100%), 74 (17) and 45 (50); benzonitrile (65%) m/z 103 (M^+ , 100%), 76 (45) and 75 (10); residue in inlet - 2%.

Pyrolysis of Dimethylformamide. 0.154g (2.11mmol), 40-60°C, 900°C, 8×10^{-3} Torr, 45 min: The pyrolysate was shown by 1H n.m.r. spectroscopy and g.c. to be unreacted starting material.

Preparation of Substituted Benzoyl Chlorides.- Thionyl

chloride (*ca.* 0.3mol) was added to the appropriately substituted benzoic acid (0.1mol) and the mixture was heated under reflux for 2h, with the exclusion of atmospheric moisture by a calcium chloride drying tube. The excess thionyl chloride was removed by distillation (b.p. 79°C) and the remaining product was purified by distillation. The following acid chlorides were made by this general method: *p*-toluoyl chloride, (71%) b.p. 120°C (50Torr), [lit.,¹⁷⁸ 102°C (15Torr)]; *o*-methoxybenzoyl chloride (83%) b.p. 150-152°C (12Torr) [lit.,¹⁷⁸ 145°C (14Torr)].

Preparation of 1-Aryl-3,3-diphenyl-2-azaprop-2-en-1-ones.

(a) Benzophenone imine A Grignard-nitrile complex was prepared by dropwise addition of benzonitrile (46.35g, 0.45mol) in dry ether (50ml) to a stirred Grignard reagent prepared from bromobenzene (78.50g, 0.50mol) and magnesium turnings (12.40g, 0.51g atom) in dry ether (300ml), followed by heating under reflux overnight. The reaction was carried out under dry nitrogen. After it had cooled to room temperature, the stirred complex was decomposed by the dropwise addition of methanol (*ca.* 100ml). Reaction was vigorous and the white solid which formed was filtered after the decomposition was complete (~40 min). The filtrate was concentrated by the removal of ether and methanol under vacuum before the product was distilled to give benzophenone imine as a pale yellow oil (54.33g, 67%) b.p. 180-182°C (30Torr) [lit.,¹⁸³ 127°C (3.5Torr)]; ν_{\max} 3250 cm⁻¹ (NH).

(b) 1-Aryl-3,3-diphenyl-2-azaprop-2-en-1-one

Benzophenone imine (0.05mol) was added to a solution of aroyl chloride (0.057mol) in pyridine (20g), and the mixture was cautiously warmed on a water bath for about 2h. The cooled mixture was then poured onto water (500ml), weakly acidified by hydrochloric acid, and the 1-aryl-3,3-diphenyl-2-azaprop-2-en-1-one was filtered off and dried over phosphorus pentoxide (at 0.5Torr). The following compounds were prepared in this way: 1,3,3-triphenyl-2-azaprop-2-en-1-one (99%) m.p. 110-111°C (lit.¹⁸⁴ 117-118°C); ν_{\max} 1660 cm^{-1} (CO); δ_{H} 7.7-6.9 (15H, m); m/z 285 (M^+ , 49%), 105 (100), 77 (72) and 51 (29); δ_{C} 178.98 (q), 167.47 (q), 136.12, 133.12 (q), 132.59, 130.65, 129.59 (q), 128.84, 128.13 and 127.96; 3,3-Diphenyl-1-p-tolyl-2-azaprop-2-en-1-one (100%), m.p. 155-157°C (from ethanol) (Found: C, 84.1; H, 5.85; N, 4.6. $\text{C}_{12}\text{H}_{17}\text{NO}$ requires C, 84.25; H, 5.7; N, 4.7%); ν_{\max} 1660 cm^{-1} (CO); δ_{H} 8.1-7.1 (14H, m), 2.34 (3H, s); m/z 299 (M^+ , 43%), 119 (100); 91 (47), 77 (24) and 51 (11); δ_{C} 179.06 (q), 167.29 (q), 143.31 (q), 136.39 (q), 130.66, 128.97, 128.04 and 21.39.

Pyrolysis of 1-Aryl-3,3-diphenyl-2-azaprop-2-en-1-one

These compounds had to be handled with care as they were prone to hydrolysis, so they were stored at -30°C.

Because the ^1H n.m.r. spectra showed signals due mainly to phenyl groups, and because the starting material was not eluted under g.c. conditions, it was difficult to determine the optimum furnace temperature. However the low solubility of the *p*-methyl compound in deuteriochloroform was found to

be a useful gauge as, at temperatures below 900°C, the solid in the pyrolysate was shown by m.s. and m.p. to be starting material.

(a) 1,3,3-Triphenyl-2-azaprop-2-en-1-one.- 0.134g, 0.47mmol, 140-160°C, 900°C, 5×10^{-3} Torr, 30 min: benzonitrile (54%) m/z 103 (M^+ , 100%), 77 (7) and 76 (40); benzophenone (15%) m/z 182 (M^+ , 39%), 105 (100) and 77 (61); biphenyl (5%) m/z 154 (M^+ , 100%), 151 (35) and 77 (6); Residue in inlet - nil.

(b) 3,3-Diphenyl-1-*p*-tolyl-2-azaprop-2-en-1-one.- 0.309g, 1.09mmol, 160°C, 900°C, 5×10^{-3} Torr, 45 min: benzonitrile (71%) m/z 103 (M^+ , 100%), 77 (6) and 76 (38); *p*-methylbenzonitrile (4%) m/z 117 (M^+ , 100%), 90 (35) and 63 (8); biphenyl (3%) m/z 154 (M^+ , 100%), 153 (16) and 152 (10); 4-methylbiphenyl (2%) m/z 168 (M^+ , 100%) 166 (21) and 152 (20); 4,4'-dimethylbiphenyl (2%) m/z 182 (M^+ , 83%), 167 (100) and 165 (39); benzophenone (6%) m/z 182 (M^+ , 39%), 105 (100) and 77 (59). Residue in inlet - 7%.

In the above pyrolysis experiments, a significant amount of a colourless liquid was present in the trap. By analogy with later experiments (page 184), this liquid is almost certainly benzene (and/or toluene), formed by hydrogen capture of the aryl radicals.

Pyrolysis of Benzophenone.- 0.309g (1.70mmol), 100°C, 900°C, 4×10^{-3} Torr, 45 min: The pyrolysate was shown by g.c. comparison with an authentic sample to be unreacted starting material.

Preparation of Monoaroylphenylhydrazides .- A solution of phenylhydrazine (0.08mol) in dry ether (20ml) was cooled to -10°C . The appropriately substituted benzoyl chloride (0.04 mol) in dry ether (20ml) was added dropwise to the stirred solution. The reaction took place instantaneously and a colourless solid formed which was filtered off and washed with water (200ml) to remove phenylhydrazine chloride. The following compounds were prepared in this way.

Monobenzoylphenylhydrazide. This compound was kindly supplied by Dr. M.McPherson. Mono-*p*-toluoylphenylhydrazide (69%), m.p. 173°C (from aqueous ethanol) (lit.,¹⁸⁵ 167.5°C). Mono-*o*-methoxybenzoylphenylhydrazide. (22%) m.p. $135-137^{\circ}\text{C}$ (Found: $M^{+} = 242.1064$. $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$ requires $M = 242.1055$); δ_{H} ($[\text{H}_6]$ -acetone) 8.1-6.8 (11H, m), and 4.09 (3H, s); m/z 242 (M^{+} , 13%), 135 (41), 92 (39) and 77 (34). There was also a significant peak at m/z 108 indicating the presence of phenylhydrazine hydrochloride in the sample. δ_{C} 165.96 (q), 157.00 (q), 149.47 (q), 132.36 (q), 130.04, 128.95, 128.49, 120.55, 118.66, 112.54 and 55.96.

Monoacetylphenylhydrazide.- Acetic acid (5.1g, 0.05mol) was added slowly to phenylhydrazine (10.8g, 0.1mol) and the mixture was stirred. Once the highly exothermic reaction had ceased, the mixture solidified slowly on cooling to give a pale brown solid (5.77g, 77%), m.p. 129°C (lit.,¹⁸⁶ 128.5°C).

Preparation of 3-Phenyl-2,3-diazaprop-2-en-1-ones.- The method devised by Dimroth and Tucker¹⁸⁷ for the preparation of these

compounds involved oxidation of a hydrazide in a two phase system, using 2,4,6-tri(4-t-butylphenyl)-phenol as a phase transfer catalyst. This phenol is not commercially available and involves a ten step synthesis for its preparation. It was therefore decided to use 2,4,6-tri(t-butyl)-phenol as the phase transfer catalyst, as this is commercially available. However, after the reaction was complete, it was found difficult to separate this catalyst from the desired product as the phenol could not be extracted into base, and co-distilled with the desired product. Finally, it was discovered that the catalyst was superfluous, because when the reaction was attempted in the absence of the phenol, it still proceeded smoothly and with good yield.

The appropriate phenylhydrazide (1mmol) was dissolved in methylene chloride (30ml) and shaken with a saturated solution of potassium ferricyanide in sodium hydroxide (2M, 25ml). The organic layer was separated, washed with water (20ml), dried (Na_2SO_4) and the solvent was removed *in vacuo*. The resulting red oil was then purified by bulb to bulb distillation, but could not be characterised by mass spectrometry as no parent ion peak was observed, but instead there was a peak at m/z (M+2) in the spectrum. The following compounds were prepared in this way: 1,3-diphenyl-2,3-diazaprop-2-en-1-one (86%), m.p. *ca.* 29°C, b.p. 128-130°C (0.2Torr) (lit.¹⁸⁷ 30°C); ν_{max} 1710 cm^{-1} (CO); m/z 212 [(M+2)⁺, 4%), 182 (6), 105 (100) and 77 (97): 3-phenyl-1-(p-tolyl)-2,3-diazaprop-2-en-1-one.- (54%), b.p. 130-133°C (0.2Torr) (Found: C, 74.8; H, 5.15; N, 12.45%. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$ requires C, 75.0; H, 5.40; N, 12.5%); ν_{max} 1705

cm^{-1} (CO); δ_{H} 8.1-7.3 (9H, m) and 2.44 (3H, s); m/z 226 [(M+2)⁺, 3%], 119 (100), 91 (40) and 77 (11); δ_{C} 181.49 (q), 151.71 (q), 145.31 (q), 132.89, 130.17, 129.22, 128.95, 127.18 (q), 128.06 and 21.44: 1-(o-methoxyphenyl)-3-phenyl-2,3-diazaprop-2-en-1-one.- (21%), b.p. 162-167°C (0.2 Torr)
 (Found: C, 69.9; H, 4.85; N, 11.8. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ requires C, 70.0; H, 5.05; N, 11.65%); ν_{max} 1690 cm^{-1} (CO); δ_{H} 8.1-6.9 (9H, m) and 3.77 (3H, s); m/z 242 [(M+2)⁺, 6%], 182 (16), 135 (100), 105 (16), 92 (35) and 77 (98); δ_{C} 182.98 (q), 160.08 (q), 152.03 (q), 135.56, 132.55, 132.40, 130.75 (q), 129.02 (2C), 122.99 (2C), 120.54, 112.15 and 55.91:
 1-methyl-3-phenyl-2,3-diazaprop-2-en-1-one.- (19%), b.p. 90-94°C (0.2 min). This compound is quoted in the literature but there are no physical constants available for comparison.
 ν_{max} 1750 cm^{-1} (CO); δ_{H} 7.9-7.3 (5H, m) and 2.42 (3H, s); m/z 150 [(M+2)⁺, 14%], 136 (10), 135 (7), 107 (19), 105 (17), 91 (29) and 77 (100).

Pyrolysis of 3-Phenyl-2,3-diazaprop-2-en-1-ones.

It was again found difficult to analyse the pyrolysates of these compounds, although the compounds themselves were easier to handle. However, the orange/red colour of these compounds was a useful indicator for starting material being present in the pyrolysate. Thus it was found that 750°C was the optimum furnace temperature for the pyrolysis.

(a) 1,3-Diphenyl-2,3-diazaprop-2-en-1-one.- 0.110g (0.52 mmol), 130°C, 750°C, $5-40 \times 10^{-3}$ Torr, 60 min: biphenyl (16%)

m/z 154 (M^+ , 100%), 153 (16) and 152 (32); benzophenone (3%) 182 (M^+ , 37%), 105 (100) and 77 (59); Residue in inlet - 3%.

This pyrolysis was then repeated on a larger scale and a colourless liquid which had been observed in the trap was collected and shown by g.c./m.s. to be benzene m/z 78 (M^+ , 100%), 77 (19) and 52 (19). However the yield of benzene in the pyrolysate could not be found due to its high volatility.

(b) 3-Phenyl-1-*p*-tolyl-2,3-diazaprop-2-en-1-one.- 0.085g (0.38mmol), 160°C, 750°C, $5-40 \times 10^{-3}$ Torr, 45 min: biphenyl (4%), m/z 154 (M^+ , 100%), 153 (34) and 151 (28); 4-methylbiphenyl (4%), m/z 168 (M^+ , 100%), 166 (56) and 152 (17); 4,4'-dimethylbiphenyl (2%) m/z 182 (M^+ , 100%), 166 (46) and 152 (8); *p*-methylbenzonitrile (trace) m/z 117 (M^+ , 100%), 116 (57) and 90 (31); Residue in inlet - nil.

(c) 1-*o*-Methoxyphenyl-3-phenyl-2,3-diazaprop-2-en-1-one.- 0.023g (0.10mmol), 160°C, 750°C, $5-30 \times 10^{-3}$ Torr, 45 min: benzaldehyde (28%) m/z 106 (M^+ , 79%), 105 (90) and 77 (100); biphenyl (2%) m/z 154 (M^+ , 100%), 152 (31) and 151 (21); Residue in inlet - 4%.

(d) 1-Methyl-3-phenyl-2,3-diazaprop-2-en-1-one.- 0.025g (0.17mmol), 110°C, 750°C, $5-20 \times 10^{-3}$ Torr, 45 min: It appeared from g.c./m.s. that biphenyl m/z 154 (M^+ , 100%), 149 (37) and 77 (8) was present, though this was not quantified.

In the above pyrolysis experiments, benzene (and/or toluene) was almost certainly present, although this was only shown to be the case in example (a). The other pyrolysis experiments were performed on a small scale only, so any benzene (and/or

toluene) would evaporate on work up.

Preparation of 5-Phenyl-1,1,4-trimethyl-1,3,5-triazapentadiene.-

(a) N-Phenylacetamidinium picrate .- Powdered aluminium chloride (13.3g, 0.1mol) was added, in small quantities over 45 min, to a mixture of acetonitrile (4.1g, 0.1mol) and aniline (9.3g, 0.1mol) so that the temperature did not rise above 90-100°C. It was attempted to stir the reaction mixture, but neither a magnetic nor a mechanical stirrer was satisfactory as both became stuck in the thick semi solid at the bottom of the flask. After the addition was complete, the mixture was kept at 100°C for 1h. The reaction product which consisted of a complex of the amidine with the catalyst was carefully decomposed by the dropwise addition of water until the vigorous reaction ceased. The amidine was liberated from the solution by the addition of an excess of sodium hydroxide (15g, 0.38mol) in water (100ml) and the mixture was extracted three times with chloroform. The organic extracts were dried (Na_2SO_4) and the solvent was removed to give a dark brown liquid (8.84g) which was immediately converted into the picrate by the addition of an excess of picric acid (in ethanol). A clean yellow solid was obtained (5.50g, 15%).

(b) 5-Phenyl-1,1,4-trimethyl-1,3,5-triazapentadiene.- N-Phenylacetamidinium picrate (1.81g, 5mmol) was suspended in methylene chloride (20ml) and sodium hydroxide (0.57g, 25mmol) in water (30ml) was added. The mixture was shaken vigorously and the organic layer was separated off. The aqueous layer

was extracted twice more with methylene chloride, the organic extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* (with a cold water-bath). The yellow/brown amidine (0.33g, 49%) was then used immediately: *N,N*-dimethylformamide diethylacetal (0.44g, 3mmol) in dioxan (1ml) was added to the amidine (0.33g, 2.5mmol) and the mixture was heated at 80°C for 2h. The dioxan and excess of acetal were removed by distillation before the product was purified by bulb to bulb distillation to give the pentadiene as a clean yellow oil (0.40g, 42%), b.p. 106-108°C (0.2Torr) (Found: C, 69.8; H, 8.0; N, 22.4%. $\text{C}_{11}\text{H}_{15}\text{N}_3$ requires C, 69.85; H, 7.95; N, 22.2%) δ_{H} 8.20 (1H, s), 7.3-6.7 (5H, m), 3.02 (6H, s) and 1.91 (3H, s); m/z 189 (M^+ , 33%), 174 (28), 134 (24), 119 (50), 118 (83), 93 (29) and 77 (100); δ_{C} 165.98 (q), 154.68, 151.51 (q), 128.61, 122.21, 121.06, 40.53, 34.57 and 19.77.

Pyrolysis of 5-phenyl-1,1,4-trimethyl-1,3,5-triazapentadiene.-

0.043g, (0.23mmol), 110-120°C, 800°C, 5×10^{-3} Torr, 30 min: 1,4-dimethylimidazole (18%) m/z 96 (M^+ , 100%), 95 (72) and 68 (43); aniline (*ca.*24%) m/z 93 (M^+ , 100%), 66 (36) and 64 (4); *N*-methylaniline (4%) (tentatively identified by a peak at δ 2.79 in the ^1H n.m.r. spectrum); 2-methylquinazoline (7%) m/z 144 (M^+ , 100%), 117 (69) and 77 (36). This was identified by and the yield calculated from the ^1H n.m.r. spectrum as no authentic sample was available. The literature¹⁸⁸ value for the methyl peak is δ 3.02 compared with a peak at δ 2.97 in the ^1H n.m.r. spectrum of the pyrolysate. No 3,3-dimethyl-1-phenyl-1,3-diazapropene could be detected, by g.c. comparison with an authentic sample.

1,4-Dimethylimidazole .- Copper acetate (30g, 0.15mol) was dissolved in a stirred solution of 20% aqueous ammonia (100ml) and formaldehyde (12.5ml, 0.16mol) was added. This was followed by methylamine hydrochloride (20g, 0.30mol) and then acetol (10g, 0.14mmol). The mixture was heated at 100°C for 15 min, then was cooled and was extracted with chloroform (2x100ml), the combined organic extracts were dried (Na_2SO_4) and the chloroform was removed *in vacuo*. The remaining dark coloured liquid was then purified by bulb to bulb distillation to give the imidazole as a colourless liquid (1.65g, 11%) b.p. 193-196°C (lit.¹⁸⁹ 195-197°C); δ_{H} 7.06 (1H, s), 6.35 (1H, s), 3.35 (3H, s) and 1.94 (3H, s).

Preparation of Ethylisoformanilide .- Triethyl orthoformate (22.2g, 0.15mol) was added to a mixture of aniline (9.4g, 0.10mol) and methanolic hydrochloric acid (0.3ml, 1mmol). The mixture was heated to boiling and a Dean and Stark trap was used to collect the ethanol as it was produced. The theoretical amount (9.5ml) was collected in 2h. The excess triethyl orthoformate was then removed [b.p. 65°C (40Torr)] before the product was distilled to give the formanilide as a colourless liquid (10.85g, 73%), b.p. 123-125°C (45Torr) [lit.¹⁹⁰ 117-118°C (40 Torr)] δ_{H} 7.70 (1H, s), 7.43-6.90 (5H, m), 4.33 (2H, q), and 1.38 (3H, t).

Preparation of N-Phenylformamidine .- Ethylisoformanilide (4.47g, 0.03mol) was added to an equimolar solution of ammonia in ethanol (3M, 10ml). The reaction was monitored by ^1H n.m.r.

spectroscopy. (It was observed that the singlet peak at $\delta 7.70$ due to the methylisoformanilide disappeared as the singlet peak at $\delta 7.65$ due to the desired product appeared). The reaction was complete after 4 days and the ethanol was removed *in vacuo* to give an impure off white solid (2.81g, 79%) m.p. $117-119^{\circ}\text{C}$ (the melting point of a difumarate salt of this base has been recorded¹⁹¹); δ_{H} 7.65 (1H, s), 7.4-6.6 (5H, m) and 5.0 (2H, br s).

Attempted Preparation of 5-Phenyl-1,1-dimethyl-1,3,5-triaza-pentadiene.- *N*-Phenylformamidine (0.36g, 3mmol) and bis-dimethylamino-*t*-butyloxymethane (1.0g, 6mmol) were stirred together and the mixture monitored by ^1H n.m.r. spectroscopy. The signal at $\delta 4.10$ due to the aminor was reduced. After 2h any *t*-butanol which may have been formed was removed by distillation (Kugelrohr) before the remaining material was purified by bulb-to-bulb distillation[b.p. $145-150^{\circ}\text{C}$ (0.2Torr)]. However no tractible material was formed.

Attempted Preparation of 1,4-Diphenyl-1,3,4-triazabutadiene.

(a) 1,4-Diphenyl-1,3,4-triazabut-1-ene .- Phenylhydrazine (1.08g, 10mmol) was added under nitrogen to a stirred solution of ethylisoformanilide (1.34g, 9mmol) and the flask became hot due to the highly exothermic reaction. After the resulting liquid had been left at -30°C for four days a solid had formed which was then filtered off, washed thoroughly with ether and recrystallised from ethanol. (0.51g, 48%) m.p. $94-96^{\circ}\text{C}$ (lit.¹⁹² m.p. of crude material $98-99^{\circ}\text{C}$).

(b) 1,4-Diphenyl-1,3,4-triazabutadiene .- 1,4-Diphenyl-1,3,4-triazabut-1-ene (1.06g, 5mmol) was dissolved in methylene chloride (40ml) and was added to a saturated solution of potassium ferricyanide in sodium hydroxide (2M, 100ml). The mixture was vigorously shaken and was extracted with methylene chloride (40ml x 3). The organic extracts were washed with water (40ml) and dried (Na_2SO_4) before the solvent was removed *in vacuo* (with a cold water bath). T.l.c. showed one main spot with a significant amount of material left on the baseline. The material was purified by chromatography on a small alumina column (10cm x 1cm) using methylene chloride as the eluent. A clean red oil was obtained, but this was shown by g.l.c. and ^{13}C n.m.r. spectroscopy to be a complex mixture.

PART 3PREPARATION OF COMPOUNDS FOR VARIABLE TEMPERATURE ^1H N.M.R.SPECTROSCOPY

These compounds were prepared specifically to study their variable temperature ^1H n.m.r. spectra. Certain other compounds, which have been mentioned in earlier parts of the experimental section, have also been studied in this way. The results of these studies are covered in the discussion section.

3-(Dimethylamino)-2-methylacrolein.- Phosphoryl chloride (17g, 0.11mol) was added slowly to a stirred solution of dimethylformamide (18.25g, 0.25mol) in ethylenedichloride (40 ml) which was cooled in ice. The solution was then further diluted with ethylenedichloride (20ml). The cooled mixture was stirred thoroughly before propionaldehyde diethylacetal (13.2g, 0.1mol) was added and the ice bath was then removed. The temperature rose to 30-35°C and the mixture was then heated to 70°C for a further 15 min. Ice (40g) was then added to the mixture and saturated potassium carbonate (~80ml) was slowly added dropwise. Ethylenedichloride was distilled from the reaction mixture and the reaction mixture was held for 15 minutes at 90-95°C, then extracted with benzene:ethanol (2:1). The combined extracts were dried (Na_2SO_4) and the solvent and unreacted dimethylformamide (8-10g) were removed (rotary evaporator). The product was purified by bulb to bulb distillation to give the acrolein as an orange liquid (0.9g, 9%) b.p. 96-100°C (0.5Torr) [lit.,¹⁰⁹ 90-100°C (0.2Torr)]; δ_{H} 8.82

(1H, s), 6.58 (1H, s), 3.14 (6H, s) and 1.91 (3H, s).

1,1,3,5,5-Pentamethyl-1,5-diazapentadienium fluorosulphonate.-

3-(Dimethylamino)-2-methylacrolein (0.56g, 5mmol) was dissolved in methylene chloride (3ml) and methyl fluorosulphonate (0.42ml, 5mmol) was added. The mixture was left to stand for 10 min before ether was added to give an oil, which slowly crystallised, and was then filtered off (0.5g). Due to the hygroscopic nature of the material it was used directly without further characterisation. The solid (0.5g) was dissolved in methanol (2ml) and an excess of dimethylamine (2.04g (3ml), 45mmol) was added. The solution was left to stand overnight before ether (15 ml) was added and the yellow pentadienium salt precipitated out (0.48g, 39%) m.p. 120-122°C (from isopropyl alcohol) (Found: C, 40.15; H, 7.15; N, 11.4. $C_8H_{17}FN_2O_3S$ requires C, 40.0; H, 7.15; N, 11.65%) δ_H ($[^2H_6]$ acetone) 7.55 (2H, s), 3.38 (12H, s) and 2.26 (3H, s).

1,1,3,5,5-Pentamethyl-1,5-diazapentadienium picrate.- The

corresponding fluorosulphonate (0.96g, 45mmol) was added to picric acid (2.5g, 11mmol) in acetone (5ml). A yellow solid formed which was filtered off (1.05g, 63%) m.p. 127-129°C (Found: C, 45.45; H, 5.1; N, 18.8. $C_{14}H_{19}N_5O_7$ requires C, 45.55; H, 5.2; N, 18.95%) δ_H ($[^2H_6]$ acetone) 7.51 (2H, s), 3.39 (6H, s) and 2.24 (3H, s).

Acetone dimethylhydrazone .- Acetone (23.2g, 0.4mol) was added dropwise with stirring to *N,N*-dimethylhydrazine (28.8g, 0.48mol). The mixture was warmed at 70°C for 4h then, after

cooling, ether (50ml) was added and the mixture was dried over calcium chloride (with stirring) overnight. The ether was removed by distillation using a vigreux column. The product (29.5g, 74%) was not distilled (lit.¹⁹³ b.p.95°C), but was shown to be pure by infra red (no carbonyl absorption) and ¹H n.m.r. spectroscopy; δ_H 2.32 (6H, s), 1.86 (3H, s) and 1.82 (3H, s).

Pyruvaldehyde-2-dimethylhydrazone .- A solution of acetone dimethylhydrazone (10g, 0.1mol) in dioxan (100ml) was cooled to 10°C and selenium dioxide (11.1g, 0.1mol) was added slowly in small portions. Due to the powerful and lingering smell of the selenium products, it was important that this complete experiment took place in a fume cupboard. After the reaction was complete (1½-2h) the red selenium suspension was filtered through a short silica column (eluted with ether - 100ml). The resulting liquid was concentrated (rotary evaporator) at 25°C, before the product was distilled (4.3g, 38%) b.p.92-94°C (25 Torr) [lit.¹⁰⁹ 65°C (16Torr)]; δ_H 9.05 (1H, s), 3.01 (6H, s) and 1.99 (3H, s).

5-Phenyl-1,1,3-trimethyl-1H-1,2,5-triazapentadienium perchlorate.-

Pyruvaldehyde-2-dimethylhydrazone (1.14g, 0.01mol) was added to a solution of anilinium perchlorate (1.96g, 0.01mol) in ethanol (4ml). After 2 min ether (50ml) was added to give the perchlorate as a bright orange solid which was filtered off and washed thoroughly with ether (2.71g, 94%) m.p.106-108°C (Found: C, 45.4; H, 5.75; N, 14.7. C₁₁H₁₆N₃ requires C, 45.6; H, 5.55; N, 14.5%) δ_H ([²H₆]acetone) 8.60 (1H, s), 7.7-7.4 (5H,

m), 3.84 (6H, s), 2.80 (1H, br s) and 2.54 (3H, s).

5-Phenyl-1,1,3-trimethyl-1,2,5-triazapentadiene.- 5-Phenyl-1,1,3-trimethyl-1*H*-1,2,5-triazapentadienium perchlorate (0.87g, 3mmol) was suspended in ether (15ml) and a solution of sodium carbonate (0.3g, 6mmol) in water (15ml) was added. The aqueous solution was shaken vigorously and further extracted with ether (15ml x 3). The combined organic extracts were dried (Na_2SO_4) and the crude product was distilled to give the pale yellow pentadiene (0.39g, 69%) b.p. 100-102°C (0.2Torr) (Found: C, 69.75; H, 7.95; N, 22.35. $\text{C}_{11}\text{H}_{15}\text{N}_3$ requires C, 69.85; H, 7.95; N, 22.22%) δ_{H} 7.99 (1H, s), 7.4-7.2 (5H, m), 2.83 (6H, s) and 2.18 (3H, s); m/z 189 (M^+ , 46%), 145 (54), 104 (90) and 93 (100).

1,1,5,5-Tetramethyl-1*H*-1,5-diazapentadienium perchlorate.-

A solution of 1,5-diphenyl-1*H*-1,5-diazapentadienium perchlorate (6.46g, 0.02mol) in methanol (50ml) was treated with an excess of dimethylamine [6.0g (10ml), 0.13mol] and was stirred overnight. Ether (150ml) was then added and the product precipitated out (4.34g, 95%) m.p. 122-124°C (lit.¹⁵² 126-128°C); δ_{H} 7.70 (2H, d), 5.41 (1H, t), 3.25 (6H, s) and 3.07 (6H, s).

Dimethylaminoacrolein.- 1,1,5,5-Tetramethyl-1*H*-1,2,5-diazapentadienium perchlorate (3.39g, 15mmol) was suspended in water (40ml) and was then added to a solution of sodium hydroxide (4.2g, 0.18mol) in water (40ml). The mixture was stirred for

3.5h and was then extracted with methylene chloride (3x50ml) and the combined organic extracts were dried (Na_2SO_4) and purified by bulb to bulb distillation (0.59g, 40%) b.p. 85-90°C (0.1Torr) (lit.,¹⁵² 85-89°C (0.1Torr)]; δ_{H} 8.94 (1H, d), 7.33 (1H, d), 4.96 (1H, dd), 3.08 (3H, s) and 2.78 (3H, s).

Attempted Preparation of 1,1,3,5,5-Pentamethyl-1,2,5-triazapentadienium Perchlorate. 5-Phenyl-1,1,3-trimethyl-1*H*-1,2,5-triazapentadienium perchlorate (0.58g, 2mmol) was dissolved in ethanol and an excess of dimethylamine [1.36g (2ml), 30mmol] was added. The mixture was stirred overnight at 5°C, then some of the solvent was evaporated and ether (30ml) was added. The beige solid which formed was filtered off and found to be dimethylammonium perchlorate.¹⁵⁰ The mother liquor was dried (Na_2SO_4), then the solvent was removed *in vacuo* to give 1,1,3-trimethyl-5-phenyl-1,2,5-triazapentadiene.

In another attempt to make the required perchlorate, dimethylamine perchlorate (0.40g, 2.75mmol) in ethanol (5ml) was reacted with pyruvaldehyde-2-dimethylhydrazone (0.28g, 2.5 mmol). The reaction was monitored by U.V. spectroscopy. After about 5 min at room temperature, the mixture was heated under reflux for about 2h. A black intractible tar was formed.

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PUBLICATIONS

**Anomalous Products from 1,2,5-Triaza- and 1,5-Diaza-pentadiene
Thermolyses: Formation of Amidines and Pyrroles, respectively**

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**Anomalous Products from 1,2,5-Triaza- and 1,5-Diaza-pentadiene
Thermolyses: Formation of Amidines and Pyrroles, respectively**

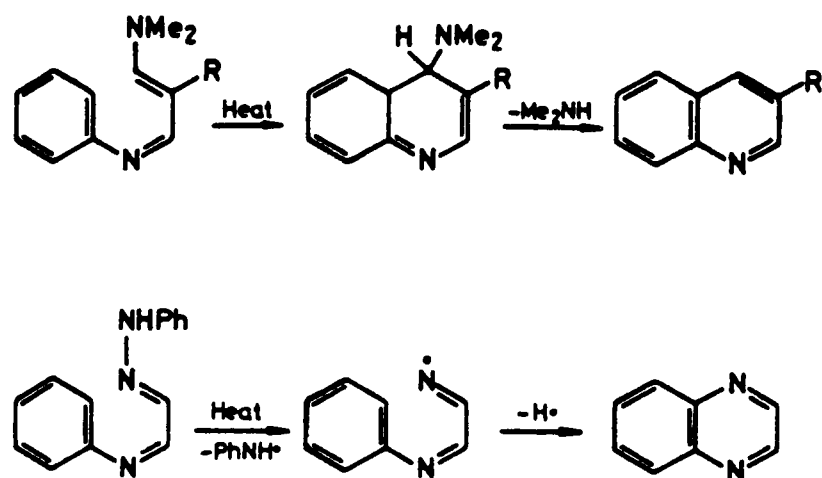
By HAMISH McNAB* and ELIZABETH-ANN MURRAY

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Summary Gas-phase thermolysis of the dimethylamino-azoalkene (1) gives the formamidine (2) by loss of HCN: in contrast, the related 1,5-diazapentadiene (4) under more forcing conditions gives aniline (30%) and *N*-methylpyrrole (43%).

THE thermal chemistry of azapentadienes is dominated by cyclisation reactions to give fused heterocycles. Jutz has shown that 3-substituted-1,5-diazapenta-1,3-dienes undergo a concerted cyclisation with elimination to give quinolines¹ while we have demonstrated that the superficially related

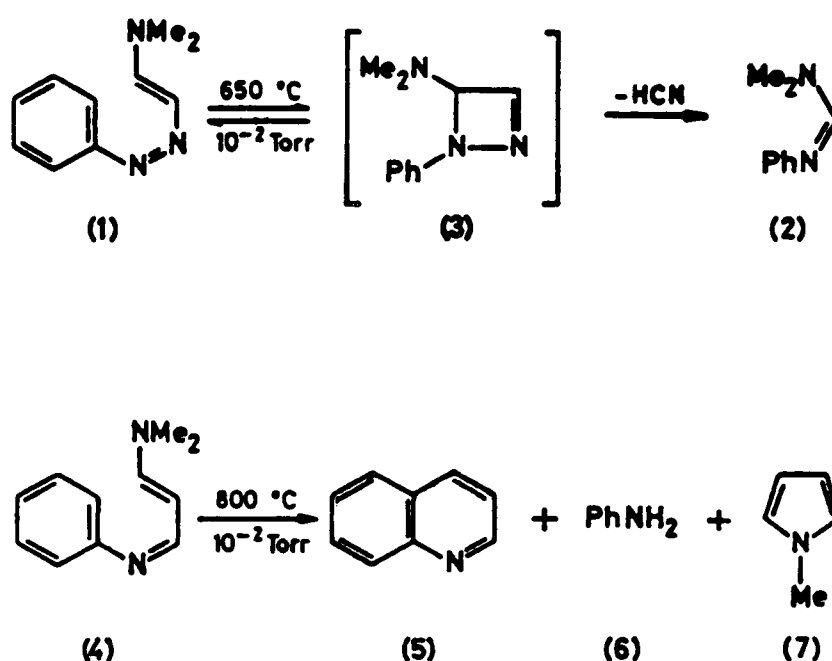
formation of quinoxalines from 1,2,5-triazapentadienes proceeds in the gas phase *via* a conjugated iminyl radical^{2,3} (Scheme 1). We now report the results of gas-phase thermolyses of related systems, in which the 1-aryl ring is not involved in the major reaction pathway.



SCHEME 1

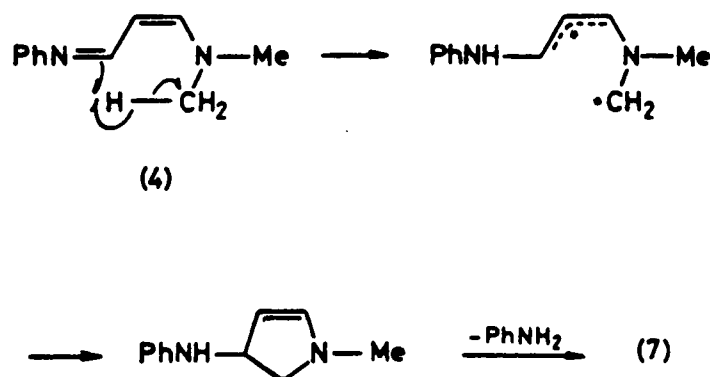
Thus, when 5,5-dimethyl-1-phenyl-1,2,5-triazapentadiene² (1) is distilled through a silica tube at 650 °C (10^{-2} Torr), the major volatile product is not cinnoline, but *NN*-dimethyl-*N'*-phenylformamidine† (2) (41%). This is most likely to be formed by concerted ring closure to the diazetine (3) followed by loss of HCN from this species. Similar reactions have been noted for other '2-azadienes,' including nitrosoalkenes,⁴ 2-azabutadienes,⁵ and azoalkenes;⁶ certain fused-ring diazetines are known to cleave to give nitriles on thermolysis.⁷ The 2-aza-group may affect the position of the heterobutadiene-heterocyclobutene equilibrium [*e.g.* (1) \rightleftharpoons (3)], but it seems more probable that the driving-force for the reaction is provided by the cleavage of the stable HCN molecule.

As expected on this basis, thermolysis of compound (4)⁸ required more vigorous conditions (800 °C at 10^{-2} Torr) and no amidines were detected in the pyrolysate. Surprisingly, quinoline (5) was present in only low yield (10%) (*cf.* Scheme 1, R = H) and the major volatile products were aniline (6) (30%) and *N*-methylpyrrole (7) (44%). This remarkable reaction, in which an *unactivated* *N*-methyl group becomes incorporated in the pyrrole ring as the C(2) unit, is to our knowledge unprecedented. The mechanism is unlikely to proceed *via* a concerted ($\sigma_2 + \pi_2$) hydrogen transfer in view of the *antarafacial* geometry required for the transition state. Intermolecular cleavage of a hydrogen atom from an *N*-methyl group is also improbable, since



SCHEME 2

thermolysis of other *NN*-dimethyl compounds under conditions similar to ours results predominantly in loss of methyl groups instead.⁹ We favour a third possible mechanism, in which an *intramolecular* hydrogen transfer to give a stabilised biradical is followed by ring closure, cleavage, and aromatisation (Scheme 2).



This reaction is general to the extent that the pyrrole system is formed in the gas phase from thermolysis of a range of 1-phenyl-5,5-dialkyl- and 1,5-dialkyl-1,5-diazapentadienes. In many cases, mixtures of pyrroles are obtained; it is not clear at present whether this results from rearrangement or cleavage of groups during the course of the reaction, or from further transformations of the pyrroles themselves.¹⁰

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† Identified by comparison (n.m.r., m.p., mixed m.p.) of its picrate derivative with an authentic sample: H. Brederick, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, 1959, 92, 837.

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Thermolysis of Polyazapentadienes. Part 6.¹ Gas-phase Cyclisation of 1,5-Diaryl-1,5-diazapentadienes: Mechanistic Aspects and some Synthetic Applications

Hamish McNab* and M. Elizabeth-Ann Murray

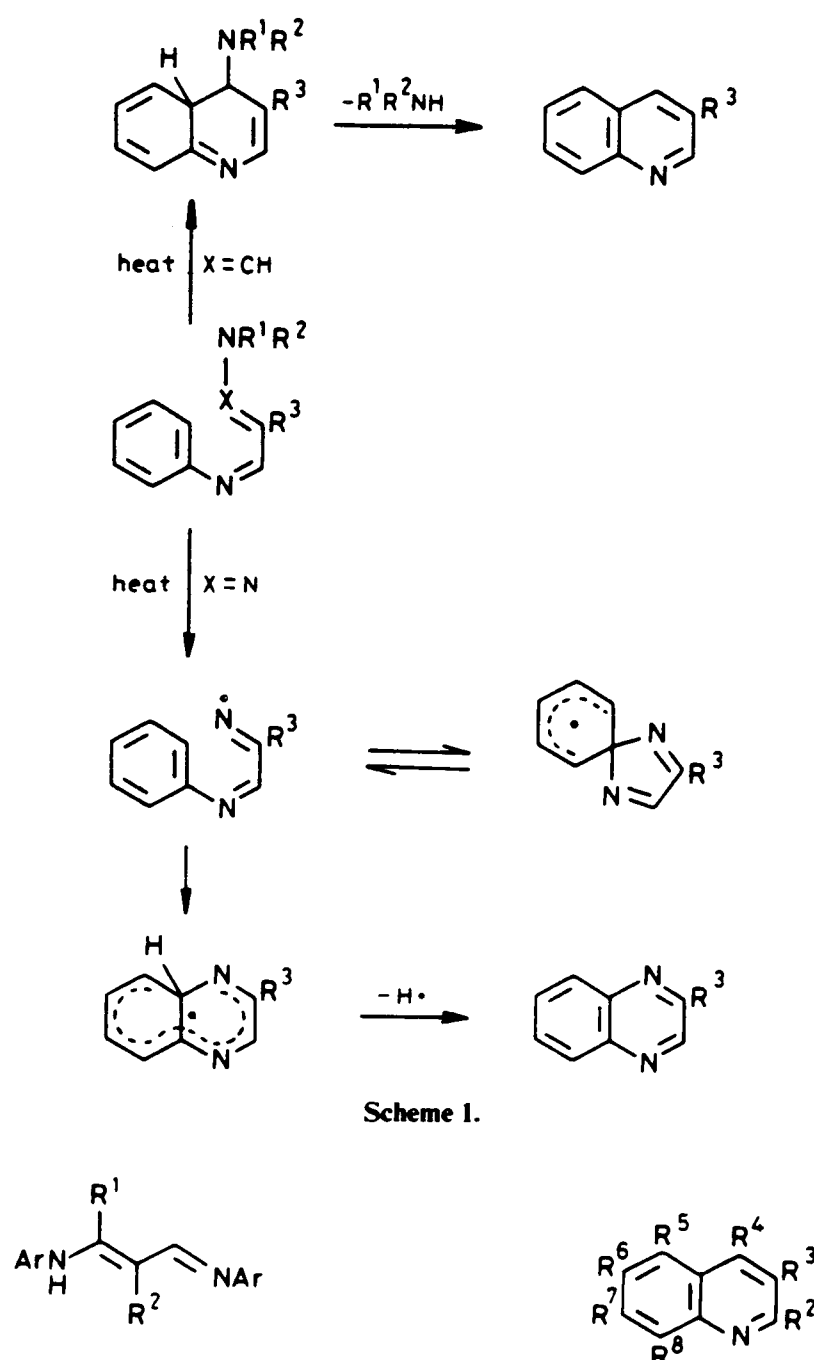
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The mode of formation of quinolines by gas-phase pyrolysis of 1,5-diaryl-1,5-diazapentadienes is contrasted with the thermal behaviour of 1,2,5-triazapentadienes. The mechanism involves concerted ring closure followed by a rapid 1,5-hydrogen shift to give a 3,4-dihydroquinoline intermediate, *e.g.* (19) or (21). Subsequent aromatisation takes place by a stepwise, free-radical process. Methylquinolines (9), (10), (12), and (13) were obtained on a preparative scale by this method.

The formation of quinolines by Lewis-acid-catalysed cyclisation of 1-aryl-1,5-diazapentadienes has been known since 1923.² More recently, the method has been developed into a useful synthesis by means of Brønsted acid,³ or base⁴ catalysis, and the mechanism under these conditions has been rationalised⁴ as an 'electrocyclic ring-closure with elimination' (Scheme 1). Our extension of this work to 5-aryl-1,2,5-triazapentadienes in the gas phase duly leads to quinoxalines, but by an iminyl radical mechanism⁵ (Scheme 1). These reactions proceed under relatively mild flash vacuum pyrolysis conditions (600–650 °C) but the yield of quinoxalines is moderate and many by-products are formed. As a consequence of the iminyl mechanism, the reactions are characterised by the effects of methyl groups at certain positions of the starting material. For example (i) a single *o*-methyl group in the 5-aryl ring is ejected;⁶ (ii) cyclisation takes place predominantly *ortho* to a *m*-methyl group;⁶ (iii) methyl groups in the side-chain are incorporated into the product, though disubstitution (in side-chain and aryl group) gives a mixture of quinoxalines due to scrambling *via* the spirodienyl radical⁷ (Scheme 1). Accordingly, we have now studied the reactions of 1,5-diaryl-1,5-diazapentadienes under flash vacuum pyrolysis conditions, with emphasis on the behaviour of methyl substituents as a diagnostic test of the concerted mechanism. In addition, these experiments have provided an authentic source of certain methylquinolines, which were required in connection with another investigation.⁸

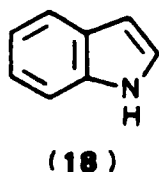
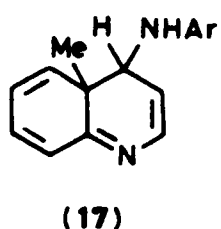
The substrates (1)–(7) were prepared as perchlorate salts by the action of the appropriate aniline on the acetal (or diacetal) of the 1,3-dicarbonyl compound, in ethanolic perchloric acid,⁹ and the free bases were liberated by standard methods. The deuterium atoms of the [²H₁₀] derivative (7) did not exchange with the medium, or scramble to other sites of the molecule under these conditions, as shown by mass spectroscopy (*M*⁺ 232) and ²H n.m.r. [δ 7.22 and 6.98 (ratio 2:3)]. The monodeuteriated derivative (8) was obtained specifically from (1) by exchange in [²H]trifluoroacetic acid.

Flash vacuum pyrolysis of 1,5-diazapentadienes requires much more vigorous conditions than the corresponding 1,2,5-triaza compound and total conversion into quinolines needs furnace temperatures of 800–850 °C. Nevertheless, these reactions give better yields of cyclised products, and analyses of the pyrolysates by g.l.c.–mass spectrometry generally show no significant volatile minor products. Pyrolysis of the di-*p*-tolyl derivative (2) gives 6-methylquinoline (10) exclusively, as shown by ¹H and ¹³C n.m.r. spectra of an isolated sample. A free-radical cyclisation might have given some 7-methylquinoline (12) *via* a spirodienyl radical (Scheme 1) and preferential C–N migration.¹⁰ Cyclisation of the di-*m*-tolyl compound (3) gives 7- and 5-methylquinoline (12) and (11) in a 2:1 ratio: a free-radical mechanism should generate the latter isomer in greater amount.⁶ In further contrast to the results for iminyl



- | | |
|---|--|
| (1) Ar = Ph, R ¹ = R ² = H | (9) R ⁸ = H |
| (2) Ar = <i>p</i> -tolyl, R ¹ = R ² = H | (10) R ⁶ = Me, R ^{8,6} = H |
| (3) Ar = <i>m</i> -tolyl, R ¹ = R ² = H | (11) R ⁵ = Me, R ^{8,5} = H |
| (4) Ar = <i>o</i> -tolyl, R ¹ = R ² = H | (12) R ⁷ = Me, R ^{8,7} = H |
| (5) Ar = Ph, R ¹ = Me, R ² = H | (13) R ⁸ = Me, R ^{8,8} = H |
| (6) Ar = Ph, R ¹ = H, R ² = Me | (14) R ² = Me, R ^{8,2} = H |
| (7) Ar = [² H ₅]Ph, R ¹ = R ² = H | (15) R ⁴ = Me, R ^{8,4} = H |
| (8) Ar = Ph, R ¹ = H, R ² = ² H | (16) R ³ = Me, R ^{8,3} = H |

cyclisation,⁶ pyrolysis of the di-*o*-tolyl derivative (4) gives 8-methylquinoline (13) (40%) with only a trace of quinoline (9) (see later) and a small amount of 4-methylquinoline (15) (4%).



The occurrence of the latter quinoline is unusual, but it may be formed by a 1,2-methyl shift during decomposition of the intermediate (17). Unexpectedly, some indole (18) was also formed in this reaction: we have previously encountered indoles in iminyl cyclisations with *two ortho*-methyl groups¹¹ and it seems likely that the aromatic substituent is again involved, though the details of the mechanism remain unclear.

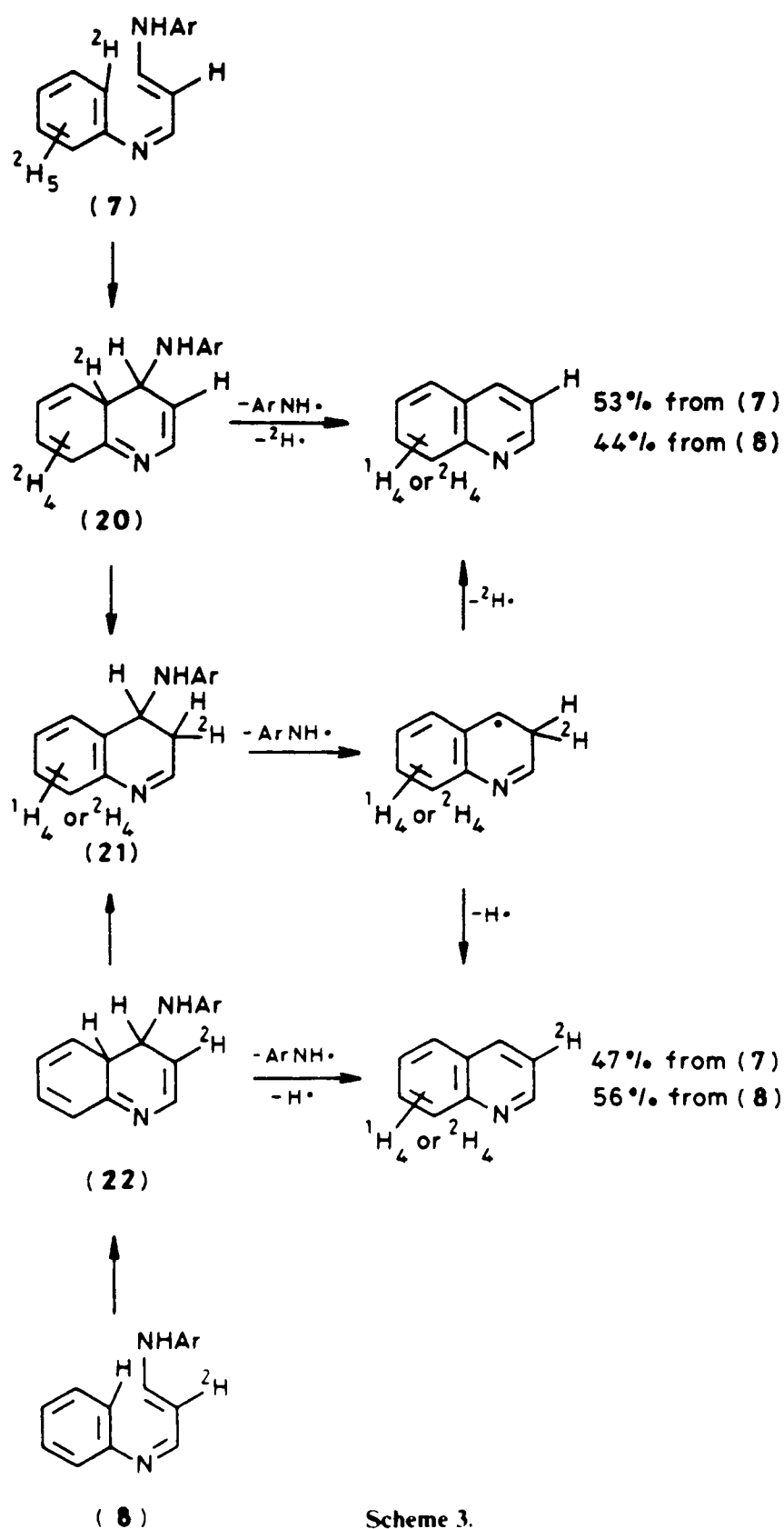
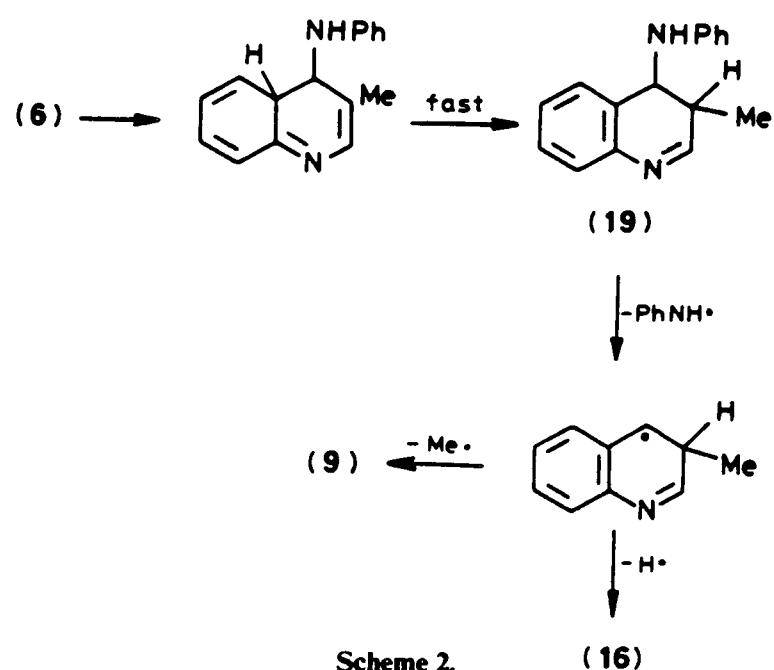
Large scale pyrolyses of (1)–(4), followed by Hinsberg separation of the aniline or toluidine,³ and purification *via* the picrate salt if necessary¹² has given pure samples of quinolines (9), (10), (12), and (13). Uncontrolled decomposition in the inlet contributes to the lower yields obtained in these preparative reactions. The use of a low molecular weight aliphatic amine as the leaving group,⁴ which would have increased the volatility of the base and also obviated the need for the Hinsberg separation, is inappropriate, because of the competitive formation of pyrroles by cyclisation on the alkyl group.¹³

The presence of a substituent on C(2) of the 1,5-diazapentadiene chain destroys the symmetry of the system and indeed both 2- and 4-methylquinolines (14) and (15) are produced, in a 4.5:1 ratio, by pyrolysis of the 2-methyl derivative (5). The major product is formed *via* the less crowded transition state.

A major distinction between the iminyl and concerted mechanisms lies in the pyrolysis behaviour of 3-methyl derivatives. Whereas 1,5-diaryl-3-methyl-1,2,5-triazapentadienes unexceptionally give 2-methylquinoxalines, the 3-methyl-1,5-diaza analogue (6) undergoes cyclisation with concomitant demethylation to give quinoline (9) (55%) with only a trace of 3-methylquinoline (16) (4%). This result suggests that Scheme 1 presents an incomplete picture of the concerted mechanism, and that the initial cyclisation is followed by a 1,5-hydrogen shift (for which the driving force is regeneration of the benzenoid system) prior to aromatisation of the heterocycle (Scheme 2). Other cases of 1,5-hydrogen shift are known in closely related cyclisations.¹⁴

We have established that the slower decomposition of (19) to give the fully conjugated species (9) or (16) takes place by a stepwise free radical mechanism (Scheme 2), since a cross-over experiment shows the existence of both arylamino and methyl radicals in the gas phase during these experiments. Thus the amine fraction obtained by co-pyrolysis of (2) and (6) consists of *N*-methyl-*p*-toluidine in addition to aniline, *N*-methylaniline, and *p*-toluidine: a separate cross-over experiment has confirmed that *N*-methylaniline and *p*-toluidine are stable under the reaction conditions. The order of arylamino and alkyl radical (or hydrogen) cleavage from (19) remains ambiguous, though the sequence of Scheme 2 is preferred for consistency with the behaviour of the parent compound (see later). The preponderance of alkyl radical over hydrogen atom cleavage is typical of a free-radical mechanism.¹⁵

We have proved that the 1,5-hydrogen shift mechanism is general, by examination of the pyrolyses of the complementary deuterium-labelled precursors (7) and (8) (Scheme 3). In both cases, the amount of migrating species ultimately incorporated at position 3 is $45 \pm 2\%$. The results are best explained by a common mechanism *via* (21), superimposed upon a 5–10% leakage by direct cleavage from (19) or (22). Since a deuterium isotope effect of *ca.* 1.4 is expected at high temperatures,¹⁶ and



none is observed,* C–H bond breaking cannot be involved in any slow step of the sequence. This is consistent with initial arylamino radical cleavage from (21), followed by rapid statistical loss of the protium or deuterium atom (Scheme 3).

This interpretation of the results suggests that the rate constants for direct cleavage from (20) or (22) are smaller by only a factor of 10–20 than that for 1,5-hydrogen shift to give (21). The formation of quinoline from the *o*-tolyl compound (4) is therefore best rationalised as a direct cleavage from (17), since sigmatropic shifts of alkyl groups are known to be very slow.¹⁸

Experimental

Unless otherwise stated, n.m.r. spectra were recorded at 100 MHz for solutions in [²H]chloroform.

1,5-Diaryl-1,5-diazapentadiene Salts and Bases.—The perchlorate salts were prepared by the action of the appropriate aniline on the 1,3-dicarbonyl compound, protected as its mono- or di-acetal, in the presence of perchloric acid.⁹ The bases were best obtained from the salts by the action of 1 mol equiv. of potassium hydroxide in methanol, as previously described for 1,2,5-triaza-derivatives.⁶

The following derivatives were prepared by these methods: 1,5-diphenyl perchlorate⁹ and base, m.p. 112–113 °C (lit.,¹⁹ 114–115 °C); *m/z* 222 (*M*⁺, 100%), 221 (91), 130 (23), and 77 (40); 1,5-di-*p*-tolyl perchlorate, m.p. 232–234 °C (lit.,¹⁹ 231–232 °C), and base, m.p. 160–162 °C (lit.,¹⁹ 164 °C), *m/z* 250 (*M*⁺, 100%), 249 (72), 144 (23), and 91 (28); 1,5-di-*m*-tolyl perchlorate (70%), m.p. 215–216 °C (from ethanol) (Found: C, 58.05; H, 5.35; N, 7.75. C₁₇H₁₉ClN₂O₄ requires C, 58.2; H, 5.4; N, 8.0%), δ_{H} ([²H₆]acetone) 10.92 (br, d), 8.76 (2 H, dd), 7.0–7.4 (8 H, complex), 6.30 (1 H, t), and 2.32 (6 H, s), and base, m.p. 78–81 °C (¹H n.m.r. identical with literature spectrum²⁰); *m/z* 250 (*M*⁺, 100%), 249 (78), 144 (24), 91 (41), and 65 (24); 1,5-di-*o*-tolyl perchlorate (84%), m.p. 209–211 °C (from ethanol) (Found: C, 58.65; H, 5.4; N, 7.75. C₁₇H₁₉ClN₂O₄ requires C, 58.2; H, 5.4; N, 8.0%), δ_{H} ([²H₆]acetone) 10.7 (br), 8.3–8.9 (2 H, complex), 7.2–7.6 (8 H, complex), 6.59 and 6.01 (1 H, 2 t), and 2.40, 2.36 and 2.32 (3 H, 3 s) (two isomers were present in 6:4 ratio), and base, b.p. 127–132 °C (0.2 Torr) (¹H n.m.r. identical with literature spectrum²⁰), *m/z* 250 (*M*⁺, 100%), 144 (90), 107 (46), and 91 (29); 2-methyl-1,5-diphenyl perchlorate²¹ and base (84%), b.p. 140–144 °C (0.1 Torr) which slowly crystallised (Found: C, 81.2; H, 6.55; N, 12.05. C₁₆H₁₆N₂ requires C, 81.3; H, 6.8; N, 11.85%), δ_{H} 11.67 (1 H, br, s), 6.8–7.5 (11 H, complex), 5.02 (1 H, d) and 1.97 (3 H, s), δ_{C} 165.79 (q), 149.58 (q), 142.78 (q), 139.05, 129.24, 128.61, 122.87, 121.81, 121.14, 115.76, 97.65, and 20.79, *m/z* 236 (*M*⁺, 100%), 235 (53), 221 (37), 145 (97), 118 (30), 93 (27), and 77 (53); 3-methyl-1,5-diphenyl perchlorate (67%; from the diethyl acetal²²), m.p. 250–252 °C (from aqueous ethanol–acetone) (Found: C, 56.9; H, 5.0; N, 8.35. C₁₆H₁₇ClN₂O₄ requires C, 57.05; H, 5.1; N, 8.3%), δ_{H} ([²H₆]DMSO) 11.12 (2 H, d), 8.58 (2 H, d), 7.1–7.6 (10 H, complex), and 2.09 (3 H, s), and base, m.p. 139–140 °C (lit.,²³ 140–141.5 °C), δ_{C} 149.94 (br, q), 146.87 (q), 129.14, 122.89, 117.72, and ca. 13 (vbr) (broad peaks are apparently associated with an exchange process, which is not apparent in the spectrum of the 2-methyl isomer), *m/z* 236 (*M*⁺, 100%), 235 (76), 218 (21), 144 (29), and 77 (64); 1,5-di([²H₅]phenyl) perchlorate (93%, from [²H₅]aniline), and base, (63%), ²H n.m.r. δ (CHCl₃) 7.22 (4 ²H, s) and 6.98 (6 ²H, s), *m/z* 232 (*M*⁺, 100%), 231 (49), 230 (95), and 82 (43).

1,5-Diphenyl-1,5-diaza[3-²H]pentadiene (Base).—The corresponding unlabelled perchlorate (0.64 g, 2 mmol) was dissolved

in [²H]trifluoroacetic acid (5 ml). This solution was neutralised with a solution of sodium deuterioxide and extracted thrice with ether. The organic extracts were dried (Na₂SO₄) and concentrated to give the [3-²H] base (0.18 g, 43%); ¹H n.m.r. showed a broad singlet at δ 8.27 and no peaks at δ < 6; *m/z* 223 (*M*⁺, 100%) and 222 (95) (there was no significant peak corresponding to [²H₂] species).

Pyrolysis Experiments.—Small-scale (0.5 mmol) pyrolyses were carried out as previously described;⁵ conditions are quoted as follows: diazapentadiene, quantity pyrolysed, inlet temperature, furnace temperature, pressure range, pyrolysis time, and yields of products [calculated from ¹H n.m.r. and confirmed by g.l.c.–mass spectrometry (5% SE30)]. Isolation of the quinoline(s) from preparative pyrolyses (10–15 mmol) was accomplished by the Hinsberg method³ since attempted chromatographic separation of the aniline was unsatisfactory. Thus, the volatile fraction from a 15 mmol pyrolysis was suspended in a solution of sodium hydroxide (2.3 g) in water (50 ml) and toluene-*p*-sulphonyl chloride (6.0 g, ca. two-fold excess) was added. The mixture was stirred at room temperature for 3 h and was then steam distilled. The distillate was saturated with sodium chloride and extracted with methylene chloride (3 × 30 ml), and the organic extracts were dried (Na₂SO₄) and concentrated. The residue was purified by bulb-to-bulb distillation at reduced pressure to give the pure quinoline. Yields are often much lower than found in the trial experiments because of significant decomposition in the inlet, and because of losses in work-up.

1,5-Diphenyl, 82.1 mg (0.37 mmol), 100–120 °C, 800 °C, 3–5 × 10^{−3} Torr, 20 min, aniline (ca. 73%), *m/z* 93; quinoline (46%), *m/z* 129; unchanged 1,5-diphenyl-1,5-diazapentadiene (*m/z* 222) was also present and so most subsequent pyrolyses were carried out at 850 °C; residue in inlet 7%. Pyrolysis of the base (3.33 g, 15 mmol) at 850 °C and 10^{−2} Torr (inlet temperature 110–120 °C) over 2.5 h gave a volatile fraction (2.08 g), a tarry involatile fraction at the exit point of the furnace (0.43 g) and a residue in the inlet (0.78 g, 23%). Hinsberg separation of the volatile fraction as before gave quinoline (0.76 g, 39%), b.p. 98–101 °C (16 Torr) (lit.,²⁴ 238 °C), δ_{H} (200 MHz) 8.61 (1 H, dd), 7.88 (1 H, d), 7.70 (1 H, d), 7.3–7.5 (2 H, complex), 7.17 (1 H, t of d), and 6.96 (1 H, dd); δ_{C} ²⁵ 149.86, 147.83 (q), 135.45, 128.93, 127.79 (q), 127.30, 125.99, and 120.53.

1,5-Di-*p*-tolyl, 103.4 mg (0.41 mmol), 110–130 °C, 850 °C, 3–5 × 10^{−3} Torr, 40 min, *p*-toluidine (75%), *m/z* 107; 6-methylquinoline (69%), *m/z* 143; residue in inlet 9%. Pyrolysis of the base (3.75 g, 15 mmol) at 850 °C and 10^{−2} Torr over 3.5 h (inlet temperature 150–170 °C) gave a volatile fraction (2.35 g) and a residue (0.74 g, 20%). Hinsberg separation of the volatiles as before gave 6-methylquinoline (0.84 g, 39%), b.p. 110–112 °C (16 Torr) (lit.,²⁶ 258 °C), δ_{H} (200 MHz) 8.68 (1 H, dd), 7.87 (1 H, d), 7.78 (1 H, d), 7.2–7.3 (2 H, complex), 7.09 (1 H, dd), and 2.30 (3 H, s); δ_{C} ²⁵ 148.86, 146.37 (q), 135.64 (q), 134.64, 131.05, 128.51, 127.71 (q), 126.01, 120.40, and 20.87.

1,5-Di-*m*-tolyl, 148.4 mg (0.59 mmol), 120 °C, 850 °C, 2 × 10^{−3} Torr, 15 min, *m*-toluidine (79%), *m/z* 107; 5- and 7-methylquinoline (37% total), *m/z* 143 (¹H n.m.r. shows that the mixture is 65% 7-methyl- and 35% 5-methylquinoline); residue in inlet > 15%. Pyrolysis of the base (3.75 g, 15 mmol) at 850 °C and 10^{−2} Torr over 1.5 h (inlet temperature 130 °C) gave only a low total yield of volatiles (1.61 g) after extensive decomposition in the inlet (residue 49%). Hinsberg separation of the volatiles gave 5- and 7-methylquinolines (0.24 g, 11% total), in ratio identical with that of the trial pyrolysis. Pure 7-methylquinoline was isolated by fractional crystallisation¹² of the mixed picrates, which were obtained on the addition of a solution of picric acid (0.8 g; wet with ethanol) in acetone to a solution of the crude mixture (0.24 g) in ether. The yellow solid (0.55 g) so

* In another case, we have obtained isotope effects of > 1.5 under flash vacuum pyrolysis conditions at 650 °C.¹⁷

obtained was recrystallised twice from ethanol (ca. 2 × 350 ml) to give 7-methylquinolinium picrate (0.16 g), m.p. 241–243 °C (lit.,²⁷ 242 °C), δ_{H} (200 MHz; [²H₆]DMSO) 9.24 (1 H, dd), 9.07 (1 H, d), 8.57 (2 H, s), 8.25 (1 H, d), 7.9–8.1 (2 H, complex), 7.79 (1 H, dd), and 2.64 (3 H, s). Treatment with base and extraction with methylene chloride gave pure 7-methylquinoline (0.05 g), b.p. 138–141 °C (16 Torr) (lit.,²⁷ 257 °C), δ_{H} (200 MHz) 8.81 (1 H, dd), 8.01 (1 H, d), 7.85 (1 H, s), 7.62 (1 H, d), 7.30 (1 H, dd), 7.23 (1 H, dd), and 2.50 (3 H, s); δ_{C} ²⁵ 150.18, 148.38 (q), 139.54 (q), 135.52, 128.63, 128.26, 127.23, 126.20 (q), 120.09, and 21.68.

1,5-Di-*o*-tolyl, 85 mg (0.34 mmol), 120–130 °C, 800 °C, 4 × 10⁻³ Torr, 45 min, aniline (trace), *m/z* 93; *o*-toluidine (40%), *m/z* 107; quinoline (trace), *m/z* 129; 8-methylquinoline (40%), *m/z* 143; 4-methylquinoline (4%), *m/z* 143; recovered starting material (12%); indole (trace), *m/z* 117; residue in inlet 5%. 3-Methylquinoline was unambiguously shown to be absent and 4-methylquinoline unambiguously shown to be present as demonstrated by ¹H n.m.r. 'spiking' experiments with authentic samples. Pyrolysis of the base (3.70 g, 14.8 mmol) at 850 °C and 3 × 10⁻³ Torr (inlet temperature 150 °C) over 3 h gave a liquid pyrolysate (2.65 g). (Residue in inlet 20%). Hinsberg separation gave a mixture of quinolines (0.99 g) from which 8-methylquinoline was obtained by recrystallisation of the picrate salt from ethanol. The picrate had m.p. 199–201 °C (lit.,²⁸ 200 °C), δ_{H} (200 MHz; [²H₆]DMSO) 9.19 (1 H, dd), 9.12 (1 H, dd), 8.51 (2 H, s), 8.14 (1 H, d), 8.05 (1 H, dd), 7.93 (1 H, br, d), 7.78 (1 H, t), and 2.77 (3 H, s).

2-Methyl-1,5-diphenyl, 82 mg (0.35 mmol), 140–150 °C, 800 °C, 5 × 10⁻³ Torr, 45 min, aniline (56%), *m/z* 93; *N*-methylaniline (trace), *m/z* 107; 2-methylquinoline (54%), *m/z* 143; 4-methylquinoline (12%), *m/z* 143; residue in inlet 3%. The quinolines were identified by g.l.c. comparison with authentic samples: the presence of 4-methylquinoline was confirmed by 'spiking' the n.m.r. solution with the authentic sample.

3-Methyl-1,5-diphenyl, 99.1 mg (0.42 mmol), 140 °C, 800 °C, 4 × 10⁻³ Torr, 45 min, aniline (49%), *m/z* 93; *N*-methylaniline (19%), *m/z* 107; quinoline (55%), *m/z* 129; 3-methylquinoline (4%), *m/z* 143; residue in inlet 4%. The minor and major quinolines were identified as before.

1,5-Di([²H₅]phenyl), 61.5 mg (0.27 mmol), 100 °C, 800 °C, 3 × 10⁻³ Torr, 45 min, residue in inlet 7%. The entire pyrolysate was dissolved in [²H]chloroform and analysed by ¹H n.m.r. at 360 MHz, which showed significant peaks at δ 8.92 (1.0 H, complex), 8.15 (1.01 H, complex) and 7.39 (0.53 H, dd), due to the 2-, 4-, and 3-protons of quinoline respectively. Deuterium incorporation at position 3 is 47%.

1,5-Diphenyl[3-²H], 71.2 mg (0.32 mmol), 100 °C, 800 °C, 4 × 10⁻³ Torr, 60 min, residue in inlet 7%. ¹H N.m.r. at 360 MHz showed complex signals due to H(2) and H(4), partially coupled to H(3), at δ 9.19 (1.0 H) and 8.70 (1.0 H). The doublet due to residual ¹H at position 3 overlapped with a doublet of triplets at δ 7.80 (1.44 H): this chemical shift was confirmed by ²H n.m.r. δ (CHCl₃) 7.83. Variation of chemical shift with concentration is well known in quinolines. Protium incorporation at position 3 is therefore 44%.

Co-pyrolysis of 1,5-di-*p*-tolyl-1,5-diazapentadiene and 3-methyl-1,5-diphenyl-1,5-diazapentadiene (for method, see ref. 5). Di-*p*-

tolyl derivative (32.5 mg, 0.13 mmol), diphenyl derivative (33.6 mg, 0.14 mmol), 150 °C, 850 °C, 3 × 10⁻³ Torr, 45 min. Residues in inlet 22% and 4%, respectively. Analysis by g.l.c. (5% Carbowax, 140 °C) showed the presence of *N*-methylaniline (*m/z* 107), aniline (*m/z* 93), *N*-methyl-*p*-toluidine (*m/z* 121), and *p*-toluidine (*m/z* 107). Assignments were confirmed by comparison with authentic samples and by g.l.c.-mass spectrometry.

Co-pyrolysis of *N*-methylaniline and *p*-toluidine. *N*-methylaniline (220 mg, 2.05 mmol), *p*-toluidine (210 mg, 1.95 mmol), 80–100 °C, 850 °C, 5 × 10⁻³ Torr, 60 min. Only starting materials were detected by g.l.c. (5% Carbowax, 130 °C).

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